Coagulation-Flocculation Studies of Wastewaters.

Cover: Fountain "Tapfere Zürcherin", Lindenhof, Zürich, Switzerland.

Promotor : dr. P.G. Fohr, emeritus-hoogleraar in de waterzuivering.
Co-promotor: dr. M. Rebhun, hoogleraar in de environmental engineering,
Technion-Israel Institute of Technology, Haifa, Israel.

J. LEENTVAAR

COAGULATION-FLOCCULATION STUDIES OF WASTEWATERS

Proefschrift
ter verkrijging van de graad van
doctor in de landbouwwetenschappen,
op gezag van de rector magnificus,
dr. C.C. Oosterlee,
hoogleraar in de veeteeltwetenschap,
in het openbaar te verdedigen
op vrijdag 16 april 1982
des namiddags te vier uur in de aula
van de Landbouwhogeschool te Wageningen.

VOORWOORD

Terugkijkend op de stage die ik in het kader van mijn studie in Zürich doorbracht, geloof ik dat de bron (zie omslag), van zowel het promoveren op zich als van het onderwerp, daar ligt. Gedurende deze tijd werd mij aangeboden aldaar een promotie-onderzoek te verrichten en kwam ik voor het eerst in aanraking met de relatie tussen afvalwater, oppervlaktewater en drinkwater. Het proefschrift dat nu voor u ligt gaat op deze aspecten in.

Allen die aan het ontstaan van dit proefschrift hebben bijgedragen wil ik met een woord vooraf bedanken.

Allereerst bedank ik mijn ouders, die mij na een fijne jeugd in de gelegenheid hebben gesteld om te studeren. Jullie warme belangstelling is mij steeds tot steun geweest.

Pien, dat promoveren ook een zaak is van veel uren maken heb jij met name moeten ervaren. Voor je interesse, de goede discussies en je stimulansen ben ik je erg dankbaar. Pieter en Bert: er komt nu een tijd dat papa in het weekeinde niet meer steeds boven zit, maar meer met jullie kan spelen.

Mijn promotor, prof. dr. P.G. Fohr, dank ik voor de gelegenheid die hij mij bood om, naast de onderwijstaak, dit onderzoek te verrichten en af te sluiten met dit proefschrift.

I would like to express my gratitude to prof. dr. Menahem Rebhun (co-promotor) whose stimulating critique was invaluable. Without his help this work would not have been possible.

Zonder de hulp van de medewerkers van de vakgroep Waterzuivering zou dit onderzoek niet mogelijk zijn geweest. Graag noem ik Theo Ywema, Rob Roersma en dhr. A. van Amersfoort met name; zonder hun assistentie zouden vele proeven niet zijn uitgevoerd en de proefinstallaties niet hebben gedraaid. Ook dr. ir. Gatze Lettinga en dr. ir. Bram Klapwijk hebben bij het onderzoek een stimulerende rol gespeeld.

Het onderzoek is opgezet in samenwerking met het ingenieurs- en architectenbureau van Hasselt en de Koning te Nijmegen en Norit N.V. te Amersfoort. Voor de samenwerking en de financiële ondersteuning ben ik hen erkentelijk.

Zeer erkentelijk ben ik de studenten René Ipema, Jan Oortgiesen, Tammo Wuite, Harry Koppers, Wilco Werumeus Buning, Evert v.d. Berg, Eddie v.d. Berg, Theo Backer en Hanneke Wolferink, die in het kader van hun doctoraal-

STELLINGEN

1. De afnemende vlokgrootte van ijzerhydroxide-vlokken in verdunde suspensies onder invloed van roeren is geen gevolg van het breken van vlokken doch van erosie van kleine deeltjes van het vlokoppervlak.

   Dit proefschrift.

2. Het vermogenskengetal van een roerder in een bak met een vierkant grondvlak wordt voor praktische toepassingen goed benaderd door het vermogenskengetal voor een ronde bak met 4 radiaal opgestelde keerschotten, waarbij de afstand tussen twee tegenoverstaande keerschotten gelijk is aan de ribbe van het grondvlak van de eerst genoemde bak.

   Dit proefschrift.

3. In Nederland wordt door de betrokken beheerders bij het onderzoek van de oppervlaktewateren nog te weinig aandacht besteed aan het meten van procesvariabelen.

   Meulen, J.H.M. v.d. (1980) Waterkwaliteitskenmerken en stofbalansen van het Grevelingenmeer over de periode 1972 - 1977. Nota Deltadienst MI-80.16.

4. Bij de taakanalyse, in het kader van een taakgeoriënteerde studieprogrammering, is het van belang ook de toekomstige taakbeoefenaren (i.e. de studenten) hierbij inspraak te verlenen. Aangezien niet iedere student beschikt over een visie op zijn beroepsloopbaan is een enquête die hieraan refereert niet het meest aangewezen middel om deze inspraak te realiseren.

   Muggen, G., Deckers, J., Holleman, J.W., Leentvaar, J. en Os, W. van (1976) Herprogrammering Milieuhygiëne Wageningen. Onderwijsresearch en Praktijk II, Delftse Universitaire Pers, Delft.

5. De berichtgeving met betrekking tot gebeurtenissen in de milieusfeer door de media is dikwijls van dien aard, dat zij niet zozeer bijdraagt tot milieubesef van het publiek, doch tot een stemming die een evenwichtig milieubeleid van de overheid in de weg kan staan.

6. Zolang men bij de prioriteitsstelling ten aanzien van de verschillende functies van water voornamelijk met in geld uit te drukken waarden werkt, zal de natuurfunctie ondergewaardeerd worden.

7. Rioolwaterzuiveringsinrichtingen en waterleidingbedrijven ontmoeten ernstige moeilijkheden indien het geproduceerde slib door de aanwezigheid van een te hoog gehalte aan bepaalde bestanddelen onder de Wet Chemische Afvalstoffen zou gaan vallen. De mogelijkheid die deze wet biedt om deze moeilijkheden te ontlopen door het bijmengen van minder gecontamineerd materaal dient te worden tegen gegaan.

8. Het betrekken van open haard hout uit eigen tuin is uit oogpunt van energiebesparing voordelig. Men wordt er twee keer warm van.

9. De bij het proefschrift gevoegde stellingen krijgen door de handzame vorm ten onrechte meer aandacht dan het proefschrift.

Proefschrift van J. Leentvaar.
Coagulation-flocculation studies of wastewaters.
Wageningen, 16 april 1982.

studie aan dit onderzoekproject meewerkten. De plezierige samenwerking met Harry Koppers en Wilco Werumeus Buning tijdens een suikerbietencampagne in Groningen wil ik hier nog eens memoreren.

De Centrale Dienst van het Biotechnicon stond mij vaak met raad en daad terzijde en wil ik hierbij dankzeggen.

Tijdens deze studie zijn de resultaten vaak besproken in de KIWA-werkgroep Menging en Vlokvorming. De open en praktijk gerichte discussies in deze werkgroep zijn voor mij van groot nut geweest.Alle leden, met name dr. ir. Jos Meijers, wil ik hiervoor bedanken.

Ik heb het op prijs gesteld, dat de Deltadienst, hoofdafdeling Milieu en Inrichting, mij in staat heeft gesteld om dit proefschrift af te ronden, ook al ligt het onderwerp niet direct op het werkgebied van deze hoofdafdeling. De hulp, die ik in de laatste fase heb gehad van de onderafdeling Water-Fysica (Arie Jongejan en Gilles Wattel), van de Rekenkamer (o.a. Paul Eilers), van Eli Birnbaum en van de Typekamer (Agnes de Hamer-Willems en Josephine Romeijn-van Straten) heb ik erg op prijs gesteld.

CONTENTS

1. GENERAL INTRODUCTION

The history of coagulation-flocculation dates from the early days of recorded history when various natural materials, such as crushed almonds and beans in Egypt, nuts in India and alum in China were used to clarify turbid waters. In these cases the coagulation-flocculation preceded sedimentation in a batch process, usually in jars or earthen vessels for individual household consumption. In 1843 James Simpson used alum experimentally in England prior to the filtration, but this combination was not practiced municipally until after the patent granted to Isaiah Hyatt in 1884 for the use of a coagulant prior to rapid filtration. The interest in physical-chemical treatment reached a peak in these years in England with almost 200 plants employing chemical treatment of raw sewage installed by 1890 (Dunbar (1954), Committee Report (1971)).

Efficient coagulation-flocculation of raw sewage followed by sedimentation removes essentially all of the suspended solids, but only 50-60 percent of the incoming biochemical oxygen demand (BOD) is related to these solids and is removed from most municipal wastewaters. As a result, mere coagulation-flocculation and settling may produce a very clear effluent but one that still has a high BOD. Because of this fact and because of the large sludge quantities generated, most of the English plants that had been using chemical treatment were converted to biological types by 1910.

However, increasing population and increasing water use has now already created, in many locations, pollution problems wich cannot be adequately solved by secondary (biological) treatment. It is inevitable that the number of these cases will increase in the future. It is also inevitable that the deliberate reuse of treated wastewaters in some countries will be necessary to meet future demands. Indirect water reuse is already commonly practiced.

Therefore the concept of physical-chemical treatment has recentely experienced another surge of interest in for instance the United States, South Africa and Israel. It appears that the increasing number of cases requiring phosphate removal and high degrees of organic removal may have already established an economical use for the concept. Other possible applications for physical-chemical treatment of raw wastewater are: some industrial wastewaters and the addition of a physical-chemical treatment system to an existing conventional sewage treatment plant in tourist resorts during the tourist season.

The purpose of physical-chemical treatment may therefore be to alleviate the pollution of a receiving water body or provide a water quality adequate for reuse, or both. The advanced wastewater treatment process may be used following, in conjunction with, or replace entirely the conventional secondary process.

Some simplified schematics as illustrative examples of physical-chemical treatment systems for application to raw sewage are given in Fig. 1 (Culp and Culp (1971)). Fig. 1 shows that coagulation-flocculation is an essential step in physical-chemical treatment systems.

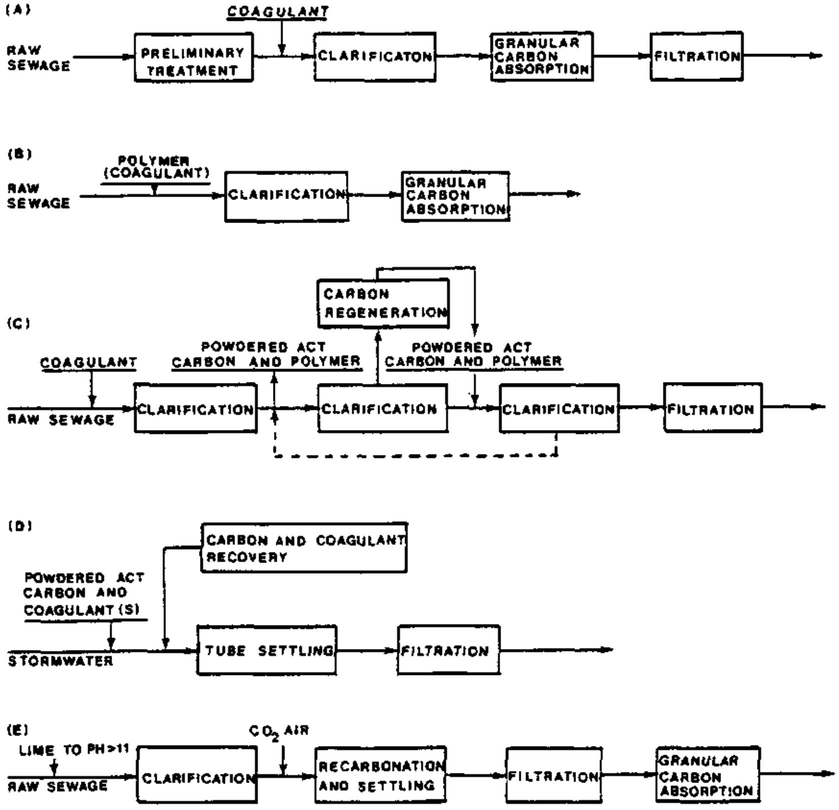

Fig. 1. Simplified schematics as illustrative examples of physical-chemical treatment systems for application to raw sewage.

The primary aim of this study was to develop a coagulation-flocculation treatment system for raw sewage of medium strength, as part of a physical-chemical treatment plant. The second aim was to elucidate some of the mechanisms involved in coagulation-flocculation of wastewater and effluent.

This study is devided in the following chapters:

A simple method to measure the power imput by an impeller in a vessel is given in chapter 2. This chapter also describes the effect of some impeller and vessel geometries on impeller power dissipation and their effect on coagulation-flocculation.

The next two chapters (3 and 4) show the effect of coagulant aid, and time and intensity of stirring on the kinetics of flocculation and on the strength of flocs.

Chapter 5 deals with the coagulation-flocculation with lime as a coagulant and gives the results of studies on the effect of Magnesium and Calcium on coagulation-flocculation of wastewater and of a synthetic sewage.

Though the capital cost of a physical-chemical wastewater plant is lower than that of a mechanical-biological plant, its recurring costs (mainly those for the coagulants) are mostly higher. Therefore it is of great importance to gain more understandig of the optimal coagulant dose in relation to the characteristics of the incoming sewage (Alaerts (1981)). This study is described in chapter 6.

Design criteria for a coagulation-flocculation plant for sewage are given in chapter 7, based on experiments with two pilot plants with a wastewater flow of 2 m^3 h^{-1} and on jar-tests.

Chapter 8 describes earlier experiments with domestic sewage carried out on batch scale and in a small scale pilot plant.

Chapter 9 is an illustration of the application of coagulation-flocculation of beet sugar wastewater and investigates the required dose of three different coagulants in two different types of pilot plants.

A definition of the terms coagulation and flocculation is needed because the terms are often used interchangeably in literature.In this study coagulation involves destabilisation of (colloidal) products and the formation of complex hydroxides. Coagulation is essentially instantaneous in that the time required is that necessary for dispersing the chemical coagulants through the liquid. Flocculation involves the bonding together of the coagulated particles to form settleable or filterable solids by agglomeration. This agglomeration is hastened by stirring the suspension to increase the collision of coagulated particles. Unlike coagulation, flocculation requires definite time intervals to be accomplished.

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2. SOME DIMENSIONLESS PARAMETERS OF IMPELLER POWER IN COAGULATION-FLOCCULATION PROCESSES

J. LEENTVAAR* and T. S. J. YWEMA

Department of Water Pollution Control, Agricultural University, Wageningen, The Netherlands.

(*Received* 1 *February* 1979)

Abstract—The simplified equation for impeller power dissipation is well known and power coefficients have been published for most impellers.

Most published data apply to cylindrical tanks with or without baffles.

This paper is a study of the effect of some impeller and vessel geometry on impeller power dissipation, especially focused on square tanks as commonly used in coagulation-flocculation processes of (waste) waters.

The experiments showed that the dimensionless Power number for a square tank can be estimated quite well by the Power number of a baffled cylindrical tank with certain dimensions.

The removal of colloidal compounds at a given *G* value differs with the type of stirrer and vessel applied. The optimal *G* value is the same for all vessel-stirrer combinations.

INTRODUCTION

Coagulation-flocculation is an essential link in the advanced (waste) water treatment process, because it removes colloidal constituents and some soluble compounds by destabilization and formation of flocs by using coagulants such as ferric chloride, hydrated lime or alum.

Coagulation-flocculation is performed in two steps. First the water flows through a rapid mixing unit, in which the waste water or surface water is mixed vigorously with the coagulant. Secondly the liquid passes a flocculator. After this the flocs are removed by settling, flotation or filtration. According to generally used kinetic formulas, the mixing intensity plays an important role in the flocculation process. TeKippe & Ham (1971) reported that a tapered velocity-gradient path (high velocity gradient at the inlet decreasing to a low value at the outlet) resulted in the greatest turbidity removals. In order to remove the maximum of the colloidal and suspended fraction the energy dissipation in the flocculator has to be designed carefully. Most flocculators consist of square tanks. The purpose of this study is to investigate the energy dissipation in square tanks and to compare this with the dissipation in cylindrical baffled and not-baffled tanks.

The significance of the *G* value for different geometric situations is investigated too.

BACKGROUND OF POWER THEORY

The power drawn by an agitator in a liquid mixing system is determined by its rotational speed and the environment in which it operates. Rushton, Costich & Everett (1950) used dimensional analysis to derive an equation, which gives the dimensionless Power number (Po) as a function of the dimensionless Reynolds number (Re), the dimensionless Froude number (Fr) and a number of dimensionless shape factors:

$$P_0 = K(\mathrm{Re})^a(\mathrm{Fr})^b(D_t/D)^c(H_1/D)^d(H_i/D)^e(P_i/D)^f(s/D)^g$$
$$\times (r/D)^h(C/D)^i(J/D)^j(W_i/D)^k(B/N_B)^l(R/N_R)^m,$$

in which:

P_0 = Power number (1).
K = Constant (1)
Re = Reynolds number (1).
Fr = Froude number (1).
D_t = Tank diameter (m).
D = Impeller diameter (m).
H_1 = Liquid height (m).
H_i = Impeller height (m).
P_i = Impeller blade pitch (m).
s = Impeller blade width (m).
r = Impeller blade length (m).
C = Height of impeller from the bottom (m).
J = Width of baffles (m).
W_i = Width of impeller blades (m).
B = Number of baffles.
N_B = Reference number of baffles.
R = Number of blades on the impeller.
N_R = Reference number for impellers.
a-m = Constant (1).

The three important dimensionless parameters are:

$P_0 = P\rho^{-1}n^{-3}D^{-5}$ (Power number)
$\mathrm{Re} = \rho n D^2 \eta^{-1}$ (Reynolds number)
$\mathrm{Fr} = n^2 D g^{-1}$ (Froude number)

in which:

P = Power consumption (Nms^{-1}).
n = Agitator speed (s^{-1}).
D = Diameter of agitator (m).
ρ = Liquid density (kgm^{-3}).
η = Dynamic viscosity of liquid (Nsm^{-2}).
g = Gravitational acceleration (ms^{-2}).

Froude's number only becomes important when the stirrer can generate a deep vortex. This condition is considered unfavourable in nearly all applications of stirring.

If geometric similarity is stipulated and a non-swirling system employed, the equation simplifies to

$$P_0 = K(\mathrm{Re})^a,$$

in which K and a are constants.

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* Present address: Min. of Transport and Public Works, Delta Dept., Env. Res. Sec., P.O. Box 439, Middelburg, The Netherlands.

For all types of stirrers the following applies for the laminar range (Re < 10):

$$P_0 = 120\,\mathrm{Re}^{-1},$$

as the liquid flow is completely controlled by viscous forces. For the turbulent range (Re > 10^4) with geometric similarity, power can be expected to be proportional to the liquid density, to the impeller speed cubed, to the diameter of the stirrer to fifth power and independent of viscosity. In this situation the Power number could be constant. In the range of Re between 10 and 10^4, "*a*" is a function of the Reynolds number.

Camp & Stein (1943) defined the *G* value, commonly used in theories on the coagulation-flocculation of (waste) water, in a stirred vessel:

$$G = \left(\frac{\epsilon}{\eta}\right)^{1/2},$$

in which

G = average velocity gradient of the fluid (s^{-1}),

ϵ = dissipated power per volume $\left(\frac{P}{V}\right)$ ($\mathrm{Nms}^{-1}\,\mathrm{m}^{-3}$),

η = dynamic viscosity (Nsm^{-2}).

For the turbulent range P is proportional to $\rho n^3 D^5$. Therefore $G\left(=\frac{P}{V\eta}\right)^{1/2}$ is proportional to $(\rho n^3 D^5)^{1/2}$. Thus the average G value is proportional to the impeller rotational speed to the 1.5*th* power.

EXPERIMENTS

Power measurements are necessary in liquid mixing to provide the data required to draw power curves. At a specific value of liquid density ρ, agitator speed n and diameter of stirrer D, the power must be measured in order to evaluate the Power number (Po):

$$Po = P\rho^{-1}n^{-3}D^{-5}.$$

The mechanical method of measuring power depends on the measurement of torque produced by a rotating agitator:

$$P = T\omega$$

in which:

P = Power (Nms^{-1}),
T = Torque (Nm),
ω = Rate of angular displacement ($= 2\pi\, n$), (s^{-1}),
n = Agitator speed (s^{-1}).

A pilot scale dynamometer was used for the determination of the dissipated energy into the water by the impeller as a function of the number of revolutions per time. Figure 1 illustrates the measuring system in which the mixing vessel was supported on a free-hanging frame. The torque produced was measured as the reaction of the vessel to the rotating agitator, the liquid acting as transmitting medium.

The displacement of the frame was kept zero by an opposite directed force generated by an adjustable current through an electro-magnetic coil fixed on the frame, freely moving around a stationary piece of iron. The current-force relation was carefully calibrated on a balance.

The impeller was driven by a Heidolph-motor on which the number of revolutions per minute could be adjusted stepless from 30 to 275 and from 300 to 2000 rev min^{-1}

Four types of stirrers were used in the experiment: a paddle (P), a small and a large two-bladed propeller (SP and LP) and a turbine (T) stirrer, as illustrated in Fig. 2.

In combination with these four stirrers, three types of vessels were used: a cylindrical tank with a diameter of 12.6 cm, a cylindrical tank with the same diameter and 4 baffles of 1.3 cm and a square tank with a cross section of 10 × 10 cm^2. See Fig. 3.

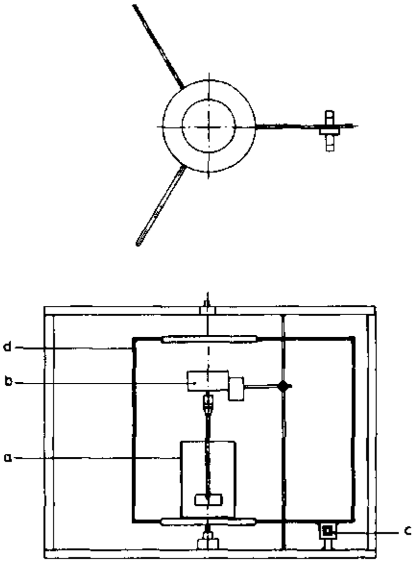

Fig. 1. Pilot scale dynamometer, (a) vessel, (b) motor, (c) coil, (d) free hanging frame.

All power measurements were carried out with 1.8 l distilled water at 20°C. All stirrers were centered in the tanks. For each combination of vessel and stirrer 3 depths of the stirrer were examined. For each geometric situation twelve different impeller speeds were applied.

With respect to significance of the *G* value, coagulation-flocculation experiments were carried out in square 2 l Plexiglass vessels with a cross section of 10 × 10 cm^2. After initial mixing with a turbine stirrer of the sewage of 10 mg Fe/l (added as 40% w/w $\mathrm{FeCl_3}$ solution) for 7 s at a *G* value of 680 s^{-1}, the sewage was flocculated at different *G* values with different impellers.

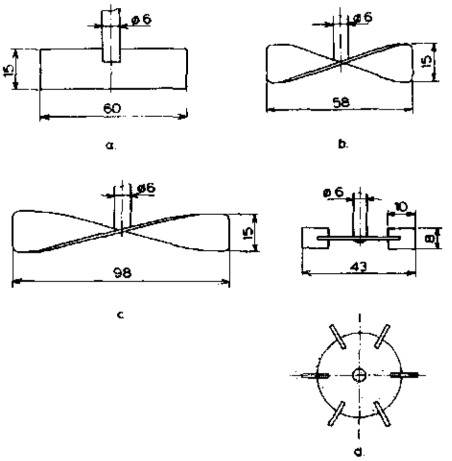

Fig. 2. Impellers used in this study: (a) paddle, (b) small propeller, (c) large propeller, (d) turbine. Size in mm.

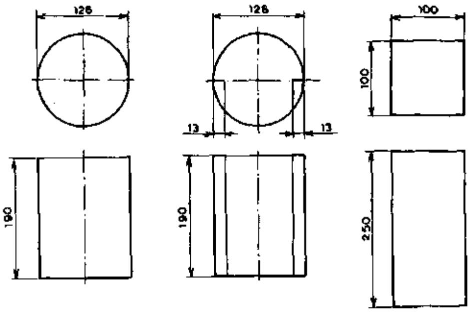

Fig. 3. Vessels used in this study. Size in mm.

In some coagulation-flocculation experiments a Couette flocculator was applied too (see Fig. 4). The Couette device employed in this work consisted of two transparent cylinders carefully centered on a stainless-steel shaft. The smaller cylinder had an outer diameter of 89.65 mm and was rigidly attached to the shaft. The larger Plexiglass cylinder had an inner diameter of 111.07 mm and was free to rotate about the axis. The annular gap provided by this geometry was 10.71 mm, while the length of the plain annular regio was 250 mm.

The length-to-gap ratio was, therefore, 23. A ratio of about 20 has been commonly used to avoid undesirable end effect in Couette devices (van Duuren, 1968).

An average G value was calculated as the G value varies with the radius R from the center. The G value was calculated according to the formula (Benze, 1967):

$$G = \frac{2\omega R_1 R_2}{R_2^2 - R_1^2}$$

in which:

G = average velocity gradient of the fluid (s^{-1})
ω = angular velocity of outer cylinder (s^{-1})
R_1 = radius of the inner cylinder (m)
R_2 = radius of the rotating outer cylinder (m)

Taylor (1923) considered a variety of circular Couette flows and found that two-dimensional flow is stable at relatively high speed of the outer cylinder rotating and the inner cylinder at rest.

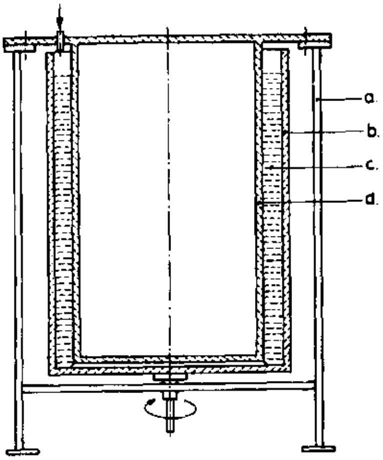

Fig. 4. The Couette flocculator. (a) frame, (b) rotating outer cylinder (diameter 111.07 mm), (c) suspension, (d) inner cylinder at rest (diameter 89.65 mm).

The Couette apparatus used in the present investigation has a distinction in that the tangential motion of the fluid results from the rotation of the outer cylinder. Both viscous and centrifugal effect exert stabilizing influences on this system. Thus the evolutionary process involving secondary flows (Taylor vortices) does not develop. The Reynolds number in this case has been defined as:

$$\mathrm{Re} = \frac{R_a \omega (R_2 - R_1) \rho}{\eta}$$

in which:

R_a = average radius $\left(= \frac{R_1 + R_2}{2} \right)$ (m)
ω = angular velocity of outer cylinder (s^{-1})
R_1 = radius of inner cylinder (m)
R_2 = radius of outer cylinder (m)
ρ = liquid density (kgm^{-3})
η = dynamic viscosity of liquid (Nsm^{-2}).

The maximal rotational speed used in flocculation experiments was $2.6\,s^{-1}$, which gave a Reynolds number of 8.8×10^3.

The critical Reynolds number above which transition from laminar to turbulent flow takes place in a geometrical similar system is about 2×10^4 (Back, 1975). Dye experiments proved that in the range of rotational speeds from 0.5 to $2.6\,s^{-1}$ as used in coagulation-flocculation experiments the flow was laminar. The flocculation period amounted, both in vessels and in the Couette apparatus, to 30 min. After flocculation, the mixture was allowed to settle. After 5 and 30 min a sample was taken at half height of the tank; its optical transmission was determined at 620 nm wavelength with cuvette diameter of 2 cm. According to previous research (Leentvaar *et al.*, 1979), there exists a high correlation between the transmission and the TOC and P content of the sample after coagulation-flocculation and sedimentation.

RESULTS

Table I summarizes the calibration of the G value (s^{-1}) with the impeller rotational speed n (s^{-1}) for the different types of impellers and vessels at impeller depth of 10 cm. The exponent for n for all combinations is close to the value of 1.5 suggested by dimensional analyses in the turbulent region.

The results in Table I were used to calculate G values in the coagulation–flocculation experiments, as

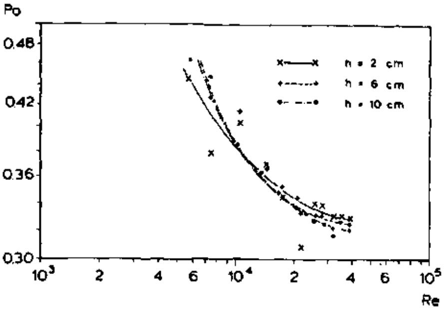

Fig. 5. The Power number (Po) as a function of the Reynolds number (Re) at different heights (h cm) of the large propeller from the bottom of the cylindrical tank.

Table 1. The relation between G value (s^{-1}) and impeller rotational speed n (s^{-1}) for different vessels and different impellers, expressed as $G = pn^q$ for 1.8 l water. Region of validity: $0.5 < n < 10$ rev s^{-1}. Distance between impeller and bottom of vessel: 10 cm. Temperature: 20°C

Impeller	Vessel	Baffles	p	q
Small propeller	Cylindrical	–	16.213	1.348
Small propeller	Cylindrical	+	18.468	1.531
Small propeller	Square		23.907	1.358
Large propeller	Cylindrical	–	38.431	1.444
Large propeller	Cylindrical	+	62.289	1.555
Large propeller	Square		56.682	1.506
Turbine	Cylindrical	–	15.574	1.256
Turbine	Cylindrical	+	18.859	1.558
Turbine	Square		19.872	1.493
Paddle	Cylindrical	–	19.728	1.428
Paddle	Cylindrical	+	32.040	1.522
Paddle	Square		32.323	1.451

Table 2. Survey of the dimensionless Power number for different vessels and different impellers at a Reynolds number of 10^4

Impeller	Cylindrical vessel without baffles	Cylindrical vessel with baffles	Square tank
Small propeller	0.5	1.0	1.0
Large propeller	0.4	1.0	0.8
Turbine	1.5	5.0	4.7
Paddle	0.7	2.6	2.0

illustrated in Fig. 7 and 8. The power dissipation experiments showed that the depth of the impeller in the tank had negligible influence on the power dissipation in the turbulent region. Figure 5 illustrates these findings for a large propeller in a cylindrical tank without baffles.

In Fig. 6 the dimensionless Power number ($Po = P/\rho n^3 D^5$) is plotted as a function of the Reynolds number ($Re = \rho n D^2/\eta$) on a log–log scale. Figure 6 shows that at Reynolds numbers greater than 10^4 the *dimensionless Power number is constant for the* square and the cylindrical baffled tank. Table 2 gives

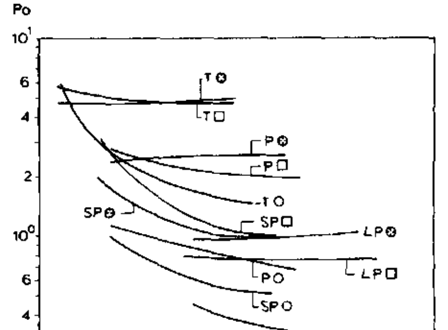

Fig. 6. The Power number (Po) as a function of the Reynolds number (Re) for paddle (P), small propeller (SP), large propeller (LP) and turbine (T) impeller in a cylindrical tank without baffles (O), with baffles (⊕) and a square tank (□). The impeller is 10 cm from the bottom of the tank.

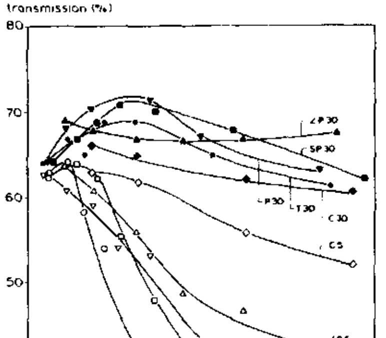

Fig. 7. Coagulation–flocculation efficiency as function of G value and type of impeller after 5 and 30 min of settling in a square tank and in a Couette flocculator (C). The symbols of the impellers are the same as in Fig. 6.

Table 3. Comparison of dimensionless Power numbers for impellers in cylindrical vessels in approximately identical geometric situation examined by different authors at Reynolds numbers of 10^4–10^5

Impeller	Baffles	Ullrich (1971)	Liepe (1966)	Present study
Small propeller	−	0.4	0.5	0.5
	+	0.9	0.9	1.0
Turbine	−	1.4	1.3	1.5
	+	4.7	5.0	5.0
Paddle	−	0.5–1.1	0.6	0.7
	+	9.2	—	2.6

a survey of the P_0 values for the different combinations of vessel and impeller at a Reynolds number of 10^4.

There are many studies on impeller power dissipation in cylindrical vessels, with or without baffles and only a few on power dissipation in square tanks. Figure 6 and Table 2 show that for a square tank, the dimensionless Power number can be estimated quite well using the Power number of a cylindrical baffled tank with a distance between two baffles equal to the length of the square tank (see Fig. 3).

Table 3 represents a comparison of dimensionless Power number for impellers in cylindrical vessels of approximately identical geometry determined by different authors at a Reynolds number of 10^4–10^5. These data show that our Power numbers are in the same range as those of the other authors mentioned here.

SIGNIFICANCE OF *G* VALUE

The significance of the *G* value for coagulation–flocculation processes is not univocal. Klute & Hahn (1974) found that the local energy dissipation of the stirrer plays an important role in the kinetics of flocculation and in the removal efficiency of suspended solids. According to Letterman *et al.* (1973), improvement in turbidity removal can be obtained by varying factors like rapid-mix intensity, rapid-mix period and concentration of coagulant. Further improvements depend on the type of impeller and vessel used.

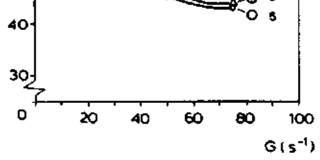

Fig. 8. The effect of the shape of the vessel on coagulation-flocculation as a function of *G* value and transmission of the sample after sedimentation during 5 and 30 min in a cylindrical tank without baffles (○), with baffles (⊕) and in a square tank (□).

Experiments were carried out in order to investigate the influence of different type of impeller and vessel on coagulation–flocculation of sewage at the same *G* value.

Coagulation–flocculation experiments were carried out with wastewater of the village Bennekom, which is mainly of domestic origin.

As an illustration of these experiments, the coagulation–flocculation performance as a function of *G* value for various impellers is plotted in Fig. 7. The increase of the *G* value caused a decline in the flocculation effect, although a *G* value of about 25 s^{-1} showed an optimal coagulation–flocculation result for all impeller types. Though the differences between the individual stirrers were small, there was an increase in flocculation effect using a turbine, a paddle, a small propeller and large propeller stirrer respectively.

The tipspeed of the impeller at the examined *G* value increases with respectively a turbine, a paddle, a large propeller and a small propeller. These two findings seem to be contradictory to each other. The results of the experiments with the Couette flocculator differ from the results with the impellers. The higher optical transmission of the sample from the Couette flocculator after 5 min leads to the conclusion that a *more uniform G value in a Couette against a G value* distribution in a stirred vessel gives compact easy settling flocs. However, the lower transmission of the sample after sedimentation for 30 min points to an advantage of a non-uniform *G* in the vessel, in order to "catch" all colloidal compounds.

The influence of the shape of the vessel on the coagulation–flocculation is illustrated in Fig. 8. The coagulation–flocculation procedure was identical to that in the previous experiments. The stirrer used for the flocculation during 30 min was a small propeller. The best results were obtained in the coagulation–flocculation experiments in the square tank. The differences between the results of the coagulation–flocculation experiments in different tanks and with different stirrers at the same average *G* value could be explained by a difference in distribution of energy input (*G*) and different tipspeeds of the impellers studied.

DISCUSSION

In general, pilot plant experiments are carried out in order to ascertain the best type of agitator and vessel geometry required to achieve a particular process result. After the process result has been satisfactorily achieved on pilot scale, the problem remains of accurately predicting the agitator speed required to obtain the same result in a geometrically similar system on full scale flocculators. It is also necessary to know the rotational speed of the full scale agitator before its power requirements can be calculated.

An individual plot of the dimensionless Power number versus the Reynolds number on log–log coordinates (power curve) is only true for a particular geometrical configuration, but is independent of vessel size.

In addition to geometrical similarity between pilot and full scale flocculator a number of other possible scale-up criteria are the following: constant Reynolds number, constant Froude number, constant Weber number, constant tip speed, constant power per unit volume and constant volumetric flow per velocity head. None of this scale-up criteria are compatible with each other.

There have been many studies on energy dissipation in stirred cylindrical tanks and only a few in stirred square tanks. The experiments showed a direct ratio between G value and the Reynolds number (Re). Also the relation between the dimensionless Power number ($Po = P/\rho n^3 D^5$) and Re was investigated. The experiments showed that for a square tank the dimensionless Power number can be estimated quite well by the Power number of a cylindrical tank with a distance between two baffles equal to the diameter of the square tank.

Coagulation–flocculation experiments with domestic sewage of the village Bennekom indicate that the coagulation–flocculation performance at a present G value differs slightly with the stirrer type and type of vessel applied.

Although the removal percentage changed somewhat with the type of stirrer and vessel applied, the optimal G value was the same for all combinations of vessel and stirrer.

The Couette flocculator results indicated that a more uniform G in a vessel is advantageous to the settling properties of the flocs and may give poorer removal of total colloidal and suspended matter.

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3. STRENGTH OF FERRIC HYDROXIDE FLOCS

J. Leentvaar[1] and M. Rebhun[2]

1. Min. of Transport and Public Works, Delta Department, Env. Res. Sec., P.O. Box 439, Middelburg, The Netherlands.
2. Division of Environmental and Water Resources Engineering, Technion-Israel Institute of Technology, Haifa, Israel.

Abstract - Strength and breakup of flocs produced in flocculation of water and effluents with ferric chloride were studied. Floc size was determined by a photographing technique and area and perimeter measurements by a Quantimet apparatus.

The experimental results obeyed the expression $d_{max} = CG^{-2\gamma}$ with $\gamma = 0.3$ for effluent and $\gamma = 0.5$ for water indicating both viscous and inertial effects in breakup. Floc strength parameter C increased with polymeric coagulant aid addition, higher C values were obtained in water than in effluent.

Floc breakup seems to take place by erosion of particles and flocs once disrupted do not grow again.

NOMENCLATURE

A	area of aggregate ((picture points)^2 or m^2)
C	floc strength coefficient in equation (7)
d	particle or aggregate diameter (m)
d_{max}	upper limit of aggregate diameter (m)
G	rms velocity gradient (s^{-1})
L	macroscale of energy containing eddies (m)
P	perimeter of aggregate (picture points or m)
p_d	pressure difference across an aggregate with diameter d (Nm^{-2})
γ	exponent in equation (5)
ε	energy dissipation per unit fluid mass (Nm s^{-1}kg^{-1})
ε_c	critical intensity of turbulence (Nm s^{-1}kg^{-1})
η	Kolmogoroff microscale (m)
λ	eddy scale (m)
ν	kinematic viscosity (m^{2}s^{-1})

τ_c yield strength of aggregate (Nm^{-2})

Ω floc volume fraction

INTRODUCTION

Although the strength of flocculated aggregates is an important design consideration for many solid-liquid separation processes in both water and wastewater treatment applications, the way in which this strength is conferred on aggregates is not well understood. Studies on the strength of flocs should include studies on the mechanisms of floc growth and floc breakup. It is, however, the balance of the opposing processes of aggregation and breakup that determines flocculator performance.

This paper attempts to develop a clearer understanding of basic floc breakup mechanisms and floc strength and draws on measurements of iron flocs in tapwater and a flocculated sewage treatment plant effluent.

THEORETICAL CONSIDERATION

Floc breakup mechanisms depend on the hydrodynamic regime, which in all practical applications in water and wastewater treatment is turbulent. Floc breakup in dilute agitated suspensions is governed by the interaction of flocs with fluid forces. Depending on its constituent materials, a floc can be viewed roughly as an aggregate of primary microparticles that are bound together to form a matrix possessing a substantial fraction of fluid within its framework.

The size and compactness of this matrix, size and shape of the microparticles, number and strength of the bonds at microparticle contacts, can all be expected to contribute to floc structure and ability to withstand disruption of fluid forces.

Parker (1972) reviewed and summarized the turbulent regime in flocculation as follows:

It is generally conceived that the overall scale of motion, or eddy scale (λ), directly determines the energy relationships characteristic of that scale. Large scale motions of scale L contain almost all of the energy and are directly responsible for energy diffusion throughout the stirring vessel by kinetic and pressure energies. However, almost no energy is dissipated by the large-scale energy-containing eddies (unless a floc is sheared between two large eddies). A scale of motion less than L is responsible for convective energy transfer to even smaller eddy scales, close to a characteristic microscale, both viscous energy dissipation and convection are the rule. The latter range of eddies has been termed the universal equilibrium range. It has been further divided into a low eddy size region, the viscous dissipation subrange, and a larger eddy size region, the intertial convection subrange. The two subranges are divided by the Kolmogoroff microscale (η), which is uniquely determined by the energy dissipation (ε) and the kinematic viscosity (ν):

$$\eta = \frac{\nu^{3/4}}{\varepsilon^{1/4}} \tag{1}$$

The relationship between ε and the more conventionally used root mean square velocity gradient (G) is (Camp and Stein (1943)):

$$G = \sqrt{\frac{\varepsilon}{\nu}} \tag{2}$$

Based on Thomas (1964), Tomi and Bagster (1978) suggested that the criterion for aggregate rupture may be expressed simply as:

$$p_d \geq \tau_c \tag{3}$$

in which p_d represents an instantaneous pressure fluctuation across a floc of size d and the term τ_c represents the limiting material strength of the unit due to the net attractive forces between member primary particles for uniform aggregates. τ_c is therefore a constant independent of aggregate size. In practice, however, τ_c may be assumed to decrease with aggregate size due to structural non-uniformities.

It is noted that, strictly, this mechanisms would only apply when inertial effects dominate: when $\eta << d << L$.

Tomi and Bagster (1978) concluded that, with these simplifying assumptions, for large aggregates ($\eta << d << L$) the force balance between aggregate strength and induced stress produced the following effect of agitation on the upper size limit of aggregates (d_{max}).

$$d_{max} \simeq \varepsilon^{-1} \text{ or } d_{max} \simeq G^{-2} \qquad (4)$$

For the case $d << \eta << L$, inertial effects are ignored over these short distances and viscous effects dominate. On simple dimensional grounds, taking into account only viscous effects, Tomi and Bagster (1978) predicted that at a critical intensity of turbulence ε_c, when $p_d > \tau_c$, all aggregates within the size range $d << \eta << L$ are ruptured. Since this behaviour is not observed in practice, Tomi and Bagster considerd an intermediate region. In many instances the size of the floc is comparable to that of the microscale so that neither the condition $d << \eta$ nor $d >> \eta$ is satisfied. Under these conditions both inertial and viscous effects are significant.

In the intermediate region, the dependence of the upper size limit, d_{max}, on the intensity of turbulence, characterised by ε, would lie intermediate between the results presented in the preceding description for large and small aggregates. A relationship suggested for this region is:

$$d_{max} \simeq \varepsilon^{-\gamma} \text{ where } 0 < \gamma < 1 \qquad (5)$$

The value of γ derived by Tomi and Bagster (1978) for this region at the critical condition when $p_d = \tau_c$, was $\gamma = 0.5$ yielding:

$$d_{max} \simeq \varepsilon^{-0.5} \text{ or } d_{max} \simeq G^{-1} \qquad (6)$$

Parker et al (1972) described two different modes of floc breakup: erosion of primary microparticles from the exterior surface layers of the floc, and fracture of the floc to form a number of smaller floc aggregates. For flocs smaller than the Kolmogoroff microscale (η), eddies in the viscous dissipation range are taken to cause floc disruption; flocs larger than η are assumed to be disrupted by turbulent eddies within the inertial subrange. For both the erosion and fracture modes Parker et al (1972) derived expressions for a maximum stable floc diameter (d_{max}), above which the flocs are unstable and subject to disruption. Flocs smaller than d_{max} are stable. The resulting expression has the form

$$d_{max} = C\ G^{-2\gamma} \qquad (7)$$

in which C is a floc strength coefficient and the exponent γ depends on both the breakup mode and size regime of eddies that cause disruption.
For erosion of flocs larger than the microscale η, Parker et al (1972) obtained the value $\gamma = 1$ in equation (7); for flocs smaller than η they obtained $\gamma = 0.5$.

EXPERIMENTS

Flocculation

Batch coagulation-flocculation tests were done in rectangular 2 l glass tanks with a cross sectional area of 10 x 10 cm^2. These experiments were carried out with tapwater as well as effluent from the wastewater treatment plant of the village Bennekom.
The following test procedure was used:

1. Mixing with a turbine type stirrer at 660 rev min^{-1}, which gave a G value of 680 s^{-1}.
2. Coagulant dose in liquid form at 660 rev min^{-1}. At the start of a 7 s period 10 mg l^{-1} Fe (as 40% w/w $FeCl_3$ solution) was added. In some experiments 3 mg l^{-1} anionic polymer Superfloc A 100 was added at the end of the 7 s period. According to the statement of the manufacturer (Cyanamid) this polymer has a molecular weight of about 5.10^6 g.
3. Flocculation for 30 min with a propeller type stirrer at fixed G values ranging from 10 to 150 s^{-1}.
4. Sedimentation for 30 min.

The G value was measured with a pilot scale dynamometer as described by Leentvaar and Ywema (1980). In turbulent flow the velocity gradient is not uniformly constant throughout the system, as in laminar flow, but fluctuating rapidly both in position and time.
During the flocculation period pictures were taken at 20 and 30 minutes.

Two batch experiments, focused on the floc strength and on the hysteresis effect, were carried out in the same reactors with tapwater using the following procedure:

1. Mixing with a turbine type stirrer at 660 rev min^{-1} (G value 680 s^{-1}).
2. Coagulant dose in liquid form at 660 rev min^{-1}. In both experiments 10 mg l^{-1} Fe was added at the start of a 7 s period, while in the second test besides ferric chloride 3 mg l^{-1} anionic polymer A 100 was added at the end of the 7 s period.
3. Flocculation with a propeller type stirrer at increasing G values, followed by decreasing G values.
   Flocculation started at a G value of 20 s^{-1}. After 2.5 and 5.0 min a picture was taken. Then every 5 minutes the G value was changed and at the end of every "5 min period" again a picture was taken. The G values successively adjusted were 40, 60, 80, 100, 120, 150, 120, 100, 80, 60, 40 and 20 s^{-1}.

Floc characterisation

Some research-workers use a Coulter Counter as a device for measuring floc sizes or floc volumes. The size or volume recorded by the Coulter Counter will be much smaller than observed optically. Using the Coulter Counter problems arise, when calculating orthokinetic flocculation kinetics, because the collision diameter, which is geometrically similar to the envelop diameter is required, and not the equivalent diameter of the solid fraction of the flocs. However, a comparison of the envelop volume and the Coulter (solid) volume would allow the water content of the floc to be calculated. In this study floc size was determined by taking pictures of the stirred suspension.

Considerable research was carried out in order to determine the best photographing technique. This technique has the advantage that no measuring device is placed into the stirred suspension and that the flocs are only subjected to the shear forces induced by the stirrer. The disadvantage of this method is that very small flocs cannot be determined and that flocs have to be individually visible. This means that a very dense floc suspension (for instance in chemical treatment of raw sewage) cannot be measured directly in this way.

The batch coagulation-flocculation tank was placed on a platform in such a

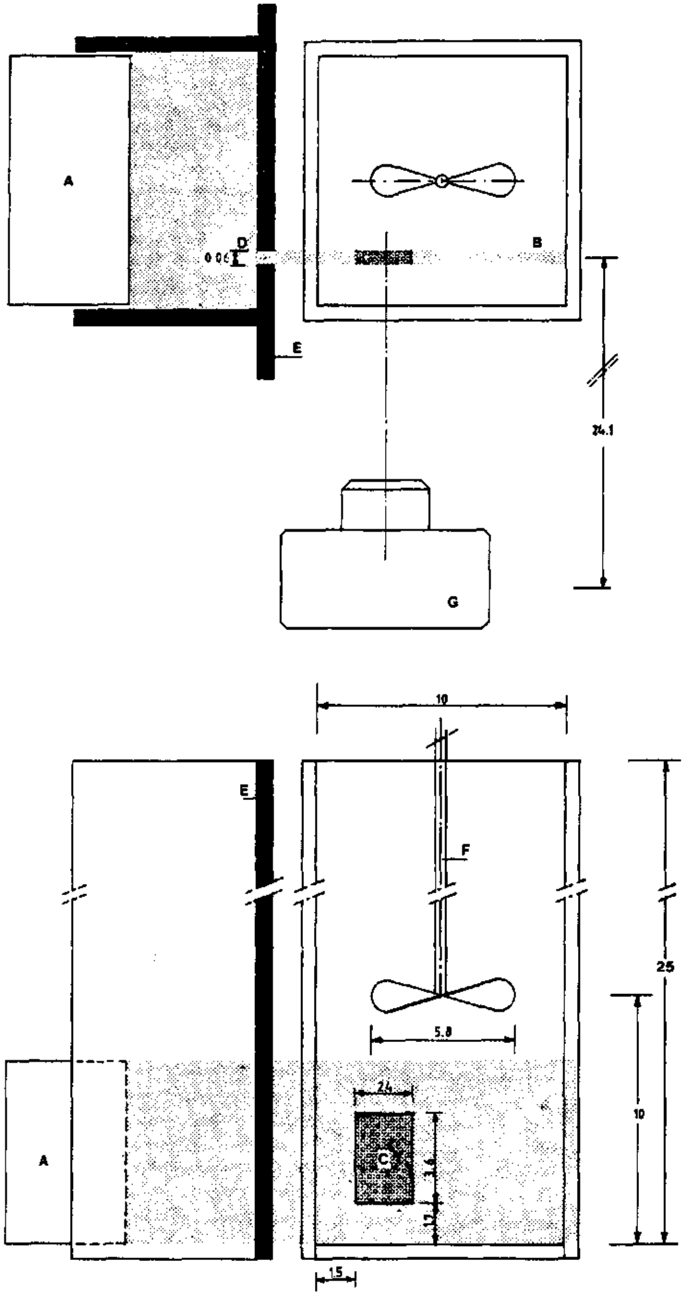

Fig. 1. Experimental set up for floc characterisation.
A: flash, B: tank, C: photographed area, D: chink of 0.06 cm,
E: black screen, F: impeller, G: photocamera. Sizes in cm.

way that pictures were taken from the front side, while a flash light illuminated only a very small section of the flocs from the side, as illustrated in Fig. 1. The camara was equipped with a macrolens (f = 55 mm, diaphragm = 8) and placed in such a way that the photographed area was equal to the negative size (24 x 36 mm). As the negatives were analysed directly on a "Quantimet 720" apparatus the negatives had to show a clear difference between the black background and the "white" flocs. This was achieved by taking all pictures in a dark room, by using only a thin layer of (flash-)light of 0.6 mm and by using a film giving an optimal black/white contrast under these circumstances. From about ten films the Ilford PANF, a 50 ASA film, gave the best results. This film was developed about 20% longer than usual. Though the shutter time of the camera was adjusted to 1/60 s, the flashtime of about 1/800 s determined the real exposure time in this case. For this reason the fast moving flocs could be photographed sharply. An example of the pictures is shown in Fig. 2.

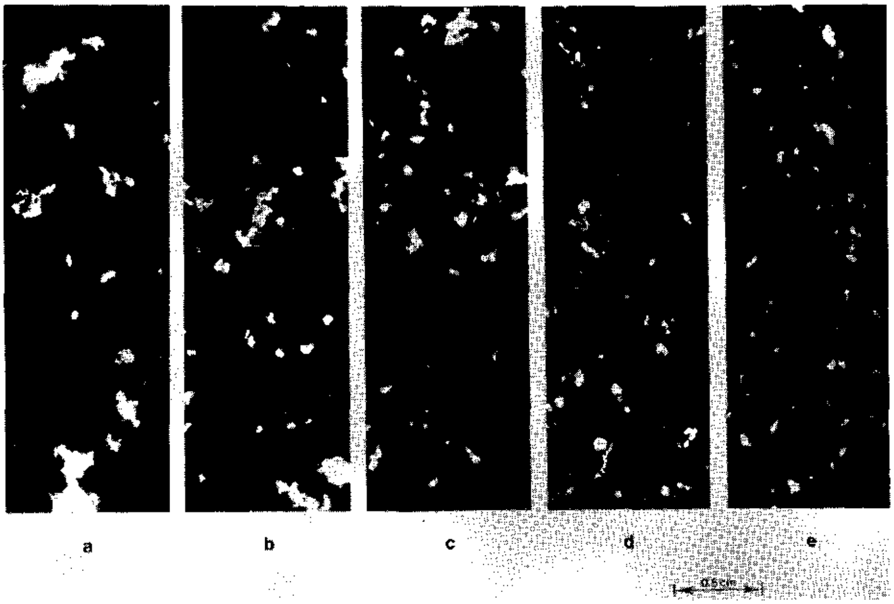

Fig. 2. Example of pictures at different G values: Tapwater + 10 mg l^{-1} Fe + 3 mg l^{-1} A100
a = 60 s^{-1}, b = 80 s^{-1}, c = 100 s^{-1}, d = 120 s^{-1}, e = 150 s^{-1}.

By means of a "Quantimet 720" the flim was analysed and from each negative at least 50 aggregates (if present) were measured. In a known area of the film negative the perimeter (P) and the corresponding area (A) of the flocs were determined. The Quantimet apparatus determines the area, the perimeter and their quotient for each particle expressed in picture points. In our experiments the length of one picture point was calibrated as $3.4 \cdot 10^{-5}$ m. The smallest detectable aggregate has an area of 2 picture points and a perimeter of 6 picture points. The "Quantimet 720" is described in detail by Williams (1971).

RESULTS AND DISCUSSION

By means of the Quantimet only the perimeter and the area of each particle are determined; therefore it was decided to take the perimeter (P) and the quotient of area and perimeter (A/P) as an indication of the diameter of the aggregate.

Careful examination of the data leads to the conclusion that in most cases the perimeter of aggregates after 30 minutes is smaller than after 20 minutes of flocculation. A plausible explanation is that if aggregates enter a region of higher energy dissipation (such as near the impeller), some ferric hydroxide polymer bridges between primary particles are broken. The polymer chains then possess greater degrees of freedom for reorientation. In many cases the polymer will no longer bridge separate particles but may simply be attached at a greater number of points on the same particle. Thus fewer bridges are available and the structure of these aggregates becomes progressively weaker and the flocs can be disrupted. Another explanation could be that gradually the polymers come to a reorientation thus excluding water molecules and resulting in a smaller floc perimeter.

In Fig. 3, 4 and 5 the values of the perimeter are divided by π in order to approximate a kind of diameter of the aggregate(s) comparable with the value of the Kolmogoroff microscale η. The microscale is calculated according to equations (1) and (2).

Linearisation of equation (5) substituting P or A/P for d_{max} and combining equation (2) gives:

$$\log P \text{ (or } A/P) = \log C - 2\gamma \log G \qquad (8)$$

Fig. 3 gives an illustration of this linearised expression in which a log-log plot of maximum P, average P and median P of the aggregates versus G in case of effluent is given. The values at $G = 10\ s^{-1}$ are not taken into account as at this G value sedimentation of flocs takes place. Fig. 3 shows that the values of P/π are in the order of magnitude of the Kolmogoroff microscale. Fig. 3 also illustrates that the slope (- 2γ) of the maximum P, the average P and the median P versus G is approximately the same for all cases. This applies to all other experiments. Linear regression shows, however, that the correlation coefficient (r) for maximum P versus G is smaller than for the latter two. This is probably due to the fact that the maximum P value was determined for only one floc measurement.

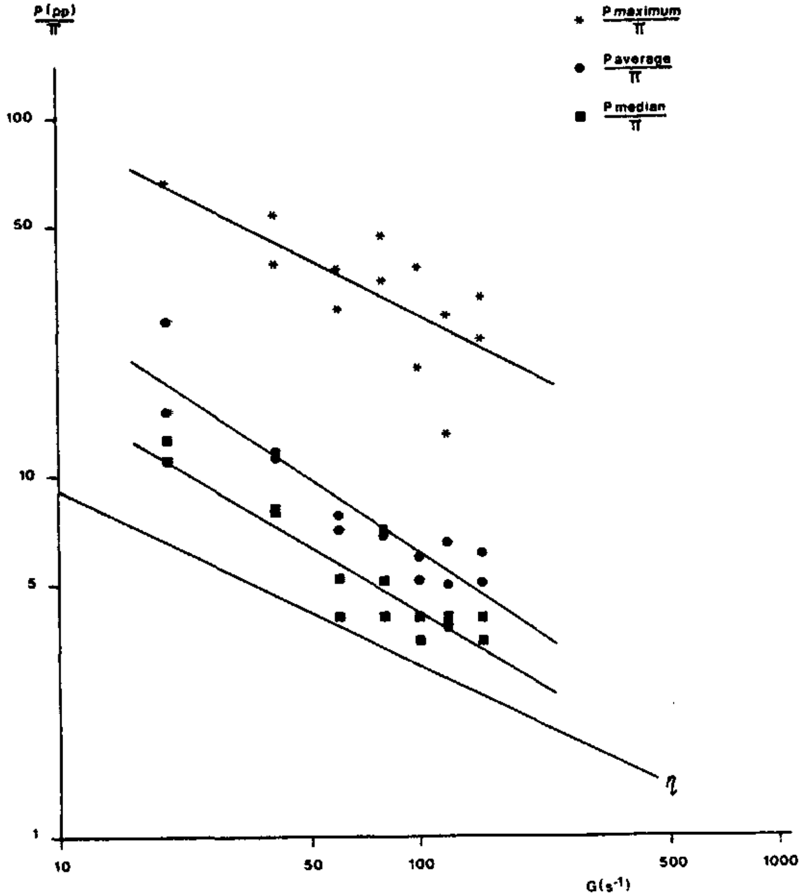

Fig. 3. Illustration of equation (8). Maximum P, average P and median P are plotted on a log-log scale versus G in case of coagulation-flocculation of effluent with 10 mg l^{-1} Fe.

Table 1 presents the values of log C and of γ as given in equation (8) for the coagulation-flocculation of effluent with 10 mg l^{-1} Fe. The average value of γ in this experiment is 0.29.

Table 1. Coagulation-flocculation of effluent with 10 mg l^{-1} Fe as coagulant. Floc strength expressed in terms of equation (8). Number of data: 14. r = correlation coefficient.

Parameter	log C	γ	r
P maximum	2.99	0.26	- 0.73
P average	2.64	0.34	- 0.93
P median	2.33	0.30	- 0.94
A/P maximum	1.31	0.25	- 0.90
A/P average	1.00	0.28	- 0.95
A/P median	0.98	0.29	- 0.94

Table 2. Average values of γ and log C (see equation (8)) for all experiments.

Effluent/ Tapwater	Coagulant dose(mg l^{-1})	Coagulant aid dose(mg l^{-1})	γ	log C
Effluent	10 Fe	-	0.29	1.87
Effluent	10 Fe	3 A 100	0.55	4.10
Tapwater	10 Fe	-	0.51	2.54
Tapwater	10 Fe	3 A 100	(0.04)	(1.40)

Table 2 summarizes the average values of γ for those experiments in which effluent or tapwater was treated with 10 mg l^{-1} Fe with or without addition of 3 mg l^{-1} anionic polymer A 100 as coagulant aid. It is not quite clear why the value of γ is very low in the case of tapwater treated with ferric chloride and a coagulant aid, although during this experiment at low G values sedimentation of flocs took place.

In Table 2 are also summarized values of log C, the floc strength coefficient. Floc strength in tapwater was higher than in effluent.
The addition of the polymeric coagulant aid caused a considerable increase in floc strength as indicated by the higher C values obtained in experiments with polymer addition. Accordingly the floc size with coagulant aid addition was significantly greater, as illustrated in Table 3.

Table 3. Median floc size, expressed as median P in picture points, for effluent and tapwater coagulation with and without coagulant aid (notation + or - poly). 1 picture point = $3.4 \cdot 10^{-5}$ m.

G (s^{-1})	Effluent		Tapwater	
	- poly	+ poly	- poly	+ poly
50	20	135	17	56
100	13	80	10	48
150	10	59	8	45

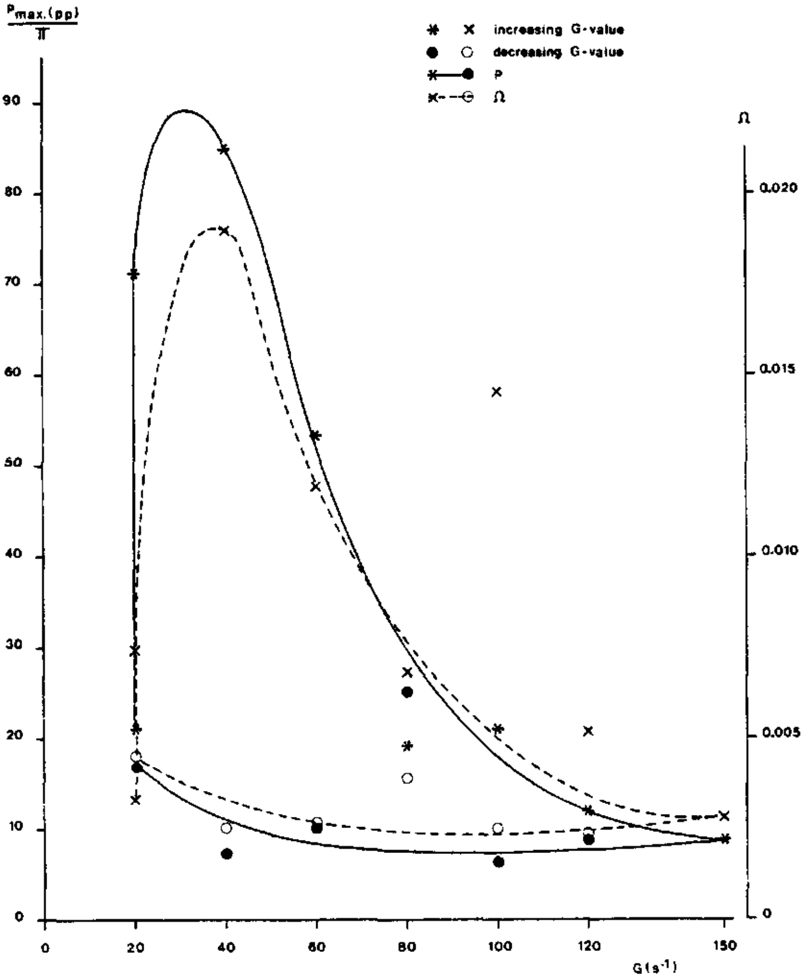

Fig. 4. Coagulation-flocculation of tapwater with 10 mg l^{-1} Fe and stepwise increasing and decreasing G values. Ω = floc volume fraction.

The γ values for effluent lie between 0 and 1, lower than suggested by Tomi and Bagster, but close to Parkers value of 0.25 for activated sludge filamentous flocs. The flocs in the effluent have some residues of the biofloc and the resistant floc may have a somewhat filamentous nature.

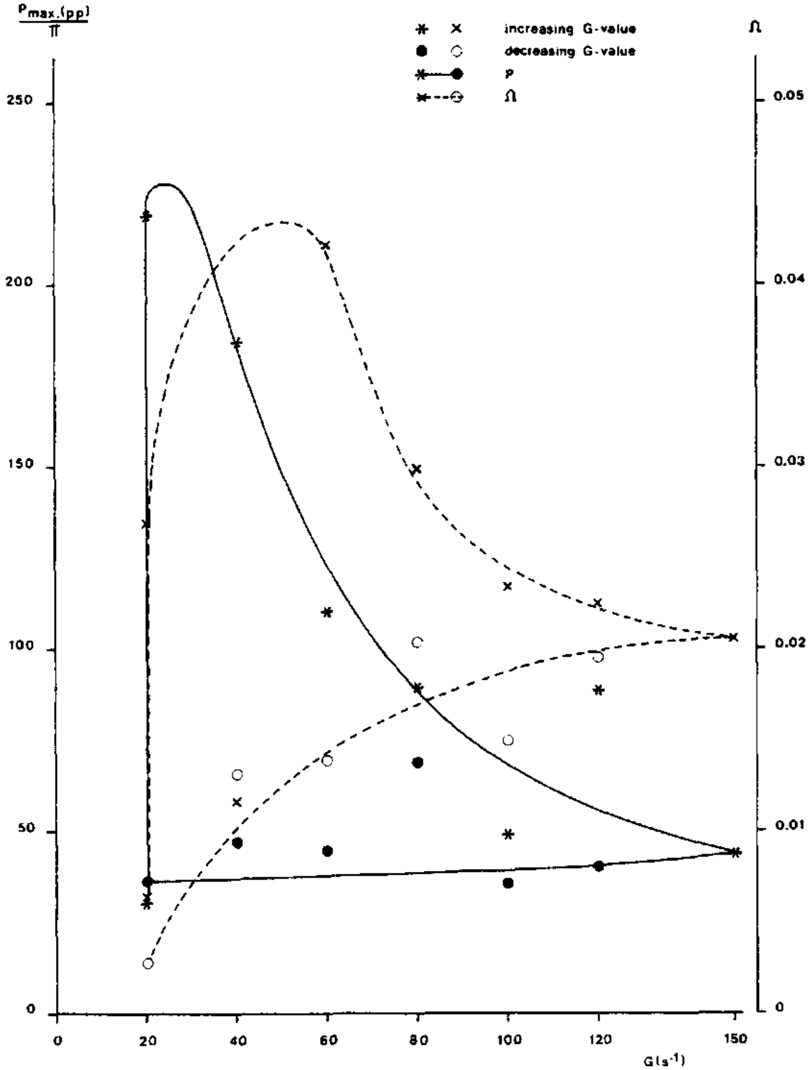

Fig. 5. Coagulation-flocculation of tapwater with 10 mg l^{-1} Fe and 3 mg l^{-1} anionic polymer A 100 as coagulant aid and stepwise increasing and decreasing G values. Ω = floc volume fraction.

The results of the two experiments with stepwise increasing and decreasing G values are given in Fig. 4 and Fig. 5. In both experiments tapwater is coagulated with 10 mg l^{-1} Fe with or without addition of a coagulant aid. Fig. 4 and Fig. 5 show that floc growth takes place during 5 to 10 minutes as P_{max} rises. Starting from $G = 40\ s^{-1}$ the floc perimeter decreases with increasing G value. Regression analysis on the data shows that the relation between floc size and the condition of agitation is also given by

$$P \simeq G^{-2\gamma} \quad \text{and} \quad A/P \simeq G^{-2\gamma} \qquad (9)$$

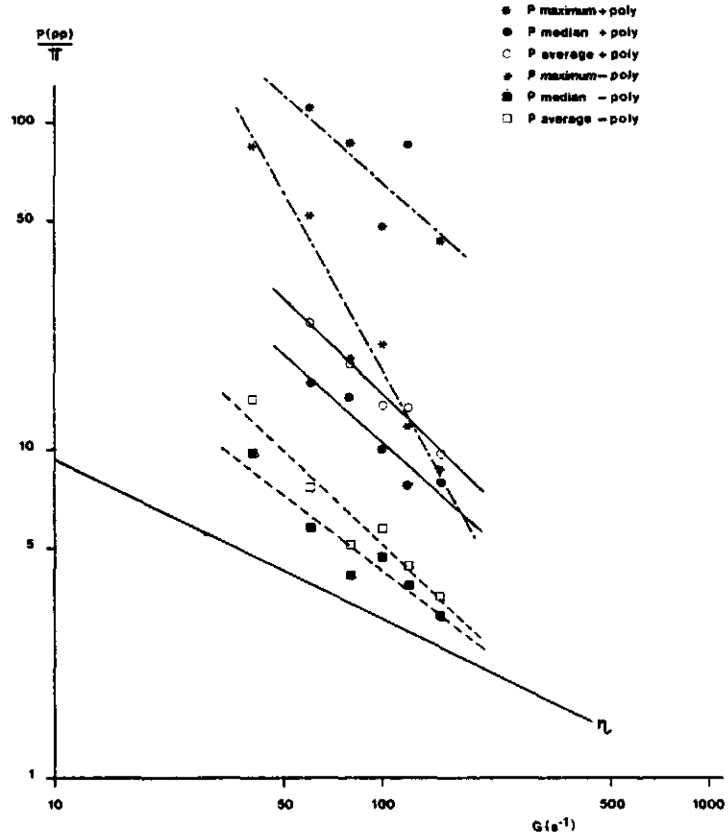

Fig. 6. Log-log plot of the data on increasing G value of Fig. 4 (without polymer addition) and Fig. 5 (with polymer addition) in case of tapwater.

in which the average value of the exponent γ for maximum, average, median P and A/P, in case of coagulation-flocculation without addition of coagulant aid, is 0.45, and with addition of 3 mg l^{-1} anionic polymer 0.42. See Fig. 6. The value of the exponent γ is in both types of experiments somewhat lower but close to the value which was determined by Tomi and Bagster (1978) for the intermediate region, where both viscous and inertial effects are significant. Table 4 summarizes the values of γ and C obtained in the experiments with stepwise increasing G values.

Table 4. Values of γ and log C (see equation (8)) for experiments with tapwater with 10 mg l^{-1} Fe as coagulant, with and without a coagulant aid and a stepwise increasing G value. Number of data:6. r = correlation coefficient.

Parameter	Coagulant aid dose (mg l^{-1})	γ	log C	r
P maximum	3 A 100	- 0.43	4.06	- 0.74
P average	3 A 100	- 0.49	3.61	- 0.99
P median	3 A 100	- 0.45	3.30	- 0.98
A/P maximum	3 A 100	- 0.42	2.43	- 0.98
A/P average	3 A 100	- 0.35	1.68	- 0.98
A/P median	3 A 100	- 0.39	1.67	- 0.99
P maximum	-	(- 0.89)	(5.30)	- 0.98
P average	-	- 0.49	3.15	- 0.96
P median	-	- 0.39	2.69	- 0.95
A/P maximum	-	- 0.37	1.80	- 0.80
A/P average	-	- 0.28	1.03	- 0.95
A/P median	-	- 0.27	0.95	- 0.96

From the number of aggregates in the detected area of the negatives, the average area of the aggregates and the detected area, the floc volume fraction Ω was calculated.

The relationship between Ω and G shown in Fig. 4 and Fig. 5 indicate that the breakup mechanism of flocs under agitation seems more likely an erosion of microparticles from the exterior surface layers of the flocs than fracture of flocs forming smaller floc aggregates, as with increasing G value the measured floc volume fraction Ω decreases which means that primary particles are formed which are not detected by the optical method used here. The size of the flocs in these two experiments, in which the G value was increased stepwise each 5 minutes is larger than after 20 and 30 minutes of flocculation at a fixed G value. This is possibly due to the same effects that cause the size reduction between 20 and 30 minutes of flocculation as described earlier.

Another important conclusion which can be drawn from Fig. 4 and Fig. 5 is that once disrupted flocs do not grow again.

CONCLUSION

The data on aggregate size (d) as a function of intensity of agitation (ε) agree with the functional form of dependence given in:

$$d \simeq \varepsilon^{-\gamma} \qquad (10)$$

in which γ ranges from 0 to 1. Floc rupture should be ascribed to the effects of hydrodynamic forces rather than those of attrition between flocs, since in all runs of this study the floc volume fraction Ω was less than 0.20. The value determined for the exponent γ ranges from 0.29 to 0.55 for floc sizes in the order of magnitude of the Kolmogoroff microscale and root mean square velocity gradients (G values) ranging from 10 to 150 s^{-1}. This value of γ is somewhat lower than, but within the range of the value that Tomi and Bagster (1978) suggested for flocs of this size.

The value of γ in equation (10) is roughly the same for all parameters that characterize floc diameter, such as maximum, average, median perimeter and maximum, average, median of the quotient of area and perimeter of the flocs.

The limited number of data do show significant difference in floc strength between effluent and tapwater.

The experiments show that treatment of water and effluent with ferric chloride and a coagulant aid leads to stronger flocs than coagulation-flocculation without polymer addition and results in 3 to 7 times larger flocs; See Table 3.

The breakup mechanism for the ferric hydroxide flocs under agitation is a surface erosion process. Once disrupted flocs do not grow again, with or without addition of coagulant aids.

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4. A CONTRIBUTION TO THE THEORY OF FLOCCULATION KINETICS

J. Leentvaar

Min. of Transport and Public Works, Delta Department, Env. Res. Sec.,
P.O. Box 439, Middelburg, The Netherlands.

Abstract - This study describes a modification of the equation for the kinetics of flocculation as used by Argaman and Kaufman. The suggestion is made to use the floc volume fraction in flocculation rate expressions instead of the particle concentration.

INTRODUCTION

Reports on flocculation kinetics studies are scattered throughout the sanitary and chemical engineering literature of the past decades (Reich and Vold (1959), Healy and La Mer (1962), Kragh and Langston (1962), Argaman and Kaufman (1970), Parker et al (1972), Bratby et al (1977), Broadway (1978), Tomi and Bagster (1978), Tambo and Watanabe (1979)). Most theoretical work has focused on determining the frequency of collisions between suspended particles in idealized systems with limited attention given to the aggregates encountered in natural water clarification or with the complex turbulent regime in stirred tanks.
The aim of this study is to further develop one of the existing theories on the kinetics of flocculation.

NOMECLATURE

a = $-C_F V^{-1} G$ in equation (7) (s^{-1})
b = $C_F K V^{-1} G - C_B P^{-1} G$ in equation (7) (s^{-1})
B = constant in equation (3) ($m^{-2}s$)
C_B = breakup constant (m)
C_F = flocculation constant (m^3)
G = root mean square velocity gradient (s^{-1})
H_{1F} = number of contacts per unit time and unit volume between primary particles and flocs ($m^{-3}s^{-1}$)

H_{ij} = number of contacts per unit time and unit volume between particles of radius R_i and R_j ($m^{-3}s^{-1}$)

K_1 = proportionality coefficient expressing the effect of the turbulence energy spectrum on the effective diffusion coefficient ($m^{-2}s$)

K_2 = performance parameter dependent on the type of stirring arrangement (m^2s^{-1})

K_3 = proportionality coefficient used with floc radius, number of flocs per unit volume and the floc volume fraction

K_4 = proportionality coefficient for floc radius and floc perimeter

K_5 = proportionality coefficient for decrease of number of primary particles per unit time and the floc volume fraction growth rate

K = mass constant

n_0 = concentration of primary particles at $t=0$ (m^{-3})

n_1 = concentration of primary particles at time t (m^{-3})

n_F = concentration of flocs (m^{-3})

n_i, n_j= concentrations of particles of radius R_i and R_j (m^{-3})

P = perimeter of particle or aggregate (picture points or m)

R_1 = radius of primary particles (m)

R_F = radius of flocs (m)

R_{ij} = radius of interaction of particles i and j (m)

t = time (of flocculation) (s)

$\overline{u^2}$ = mean square fluctuating velocity in a turbulent regime (m^2s^{-2})

V = volume of the tank (m^3)

Z = integration constant (see equation (7))

α = fraction of particle collissions resulting in lasting aggregation

Ω = floc volume fraction

PREVIOUS STUDIES ON FLOCCULATION KINETICS

The early theories of flocculation kinetics were developed by Smoluchowski (1917) who derived the basic expressions for collision frequencies under Brownian motion and laminar flow regimes. Camp and Stein (1943) were the first to realize that for practical reasons turbulent flocculation was of importance in water treatment. They generalized Smoluchowski's equation to include turbulent flow conditions by defining a root mean square velocity gradient, G, which they substituted for the well-defined velocity gradient existing in laminar flow. This leads to the following equation:

$$H_{ij} = \frac{4}{3} n_i n_j R^3_{ij} G \qquad (1)$$

where

H_{ij} = the number of contacts per unit time and unit volume between particles of radius R_i and R_j ($m^{-3}s^{-1}$)

n_i, n_j = concentrations of particles of radius R_i and R_j (m^{-3})

R_{ij} = radius of interaction of the two particles, i.e. the distance between centres of two particles forming a lasting contact (m)

G = root mean square velocity gradient (s^{-1})

The principal objection to the use of the average velocity gradient, G, is that it does not describe the length scale over which local velocity gradients extend. That is, velocity gradients which extend for a given mixing length do not influence the flocculation of particles which are larger than this distance.

Argaman and Kaufman (1970) proposed a diffusion model for orthokinetic flocculation. It is based on the hypothesis that particles suspended in a turbulent regime experience a random motion resembling gas molecules. In their analysis a simplified bimodal floc size distribution comprising primary particles and large flocs was assumed. Their expression of the rate of collision of primary particles and flocs is given by:

$$H_{1F} = 4\pi K_1 R_F^3 n_1 n_F \overline{u^2} \qquad (2)$$

where

H_{1F} = the number of contacts per unit time and unit volume between primary particles and flocs ($m^{-3}s^{-1}$)

K_1 = proportionality coefficient expressing the effect of the turbulence energy spectrum on the effective diffusion coefficient ($m^{-2}s$)

R_F = radius of flocs (m)

n_1,n_F = concentrations of primary particles and flocs respectively (m^{-3})

$\overline{u^2}$ = mean square velocity fluctuation, which is related to the root mean square velocity gradient, G, and is a measure of the intensity of turbulence (m^2s^{-2})

It was recognized by Argaman and Kaufman (1970) that two opposing processes are responsible for the change in particle concentration during flocculation, that is, aggregation of primary particles and small flocs to form larger flocs (as described by equation (2)) and the breakup of flocs into smaller fragments. This breakup mechanism is described by the rate of formation of primary particles by shearing from the floc surface:

$$\frac{dn_1}{dt} = B\ R_F^2\ R_1^{-2}\ n_F\ \overline{u^2} \qquad (3)$$

where

B = constant ($m^{-2}s$)

R_1 = radius of primary particles (m).

This surface erosion concept used by Argaman and Kaufman was proved by research on floc strength by Leentvaar (1982). The rate of change in concentration of primary particles is ths given by equations (2) and (3):

$$-\frac{dn_1}{dt} = 4\pi\ \alpha\ K_1 R_F^3\ n_1 n_F\ \overline{u^2} - B\ R_F^2\ R_1^{-2}\ n_F\ \overline{u^2} \qquad (4)$$

where

α = fraction of particle collisions resulting in lasting aggregation (1)

Argaman and Kaufman applied equation (4) to the case of a single completely mixed continuous stirred reactor, at steady state, obtained the following equation:

$$\frac{n_0}{n_1} = \frac{1 + 4\pi\alpha K_1 R_F^3 n_F \overline{u^2} t}{1 + B R_F^2 R_1^{-2} n_F n_0^{-1} \overline{u^2} t} \qquad (5)$$

where

n_0 = concentration of primary particles at time t=0 (m^{-3})

n_1 = concentration of primary particles at time t (m^{-3})

With some slight modification equation (5) was also used for a series of continuous stirred tank reactors, assuming that the floc volume fraction was constant. This assumption is questionable.

MODEL FOR TURBULENT FLOCCULATION

In order to develop a more general working equation the following assuptions were made:

1. The mean square fluctuating velocity fluctuations can be estimated from the root mean sqaure velocity gradient as follows

   $\overline{u^2} = K_2G$

   where

   K_2 = performance parameter dependent on the type of stirring arrangement and referred to as "stirrer performance coefficient" (m^2s^{-1})

2. A fixed relation exists between number of flocs, floc radius (R_F) and the floc volume

   $K_3 \Omega = R^3{}_F n_F$

   where

   Ω = floc volume fraction (1)

   K_3 = constant (1)

3. The perimeter (P) is proportional to the floc radius (R_F)

   $R_F = K_4P$

   where

   K_4 = constant (1)

4. The decrease in number of primary particles is proportional to the increase of the floc volume fraction

   $\frac{-dn_1}{dt} = K_5 \frac{d\Omega}{dt}$

   where

   K_5 = constant (m^{-3})

5. $4\pi\alpha K_1K_2K_3K_5{}^{-1} = C_F$

   where

   C_F = flocculation constant (m^3)

6. $BK_2K_3R_1{}^{-2}K_4{}^{-1}K_5{}^{-1} = C_B$

   where

   C_B = breakup constant (m)

7. The sum of floc volume fraction and primary particles times reactor volume is constant

   $\Omega + Vn_1 = K$

   where

   V = volume reactor (m^3)

   K = mass constant (1)

These assumptions lead to the following equation

$$\frac{d\,\Omega}{dt} = C_F\ (K - \Omega)\,\Omega\, V^{-1}G - C_B\,\Omega P^{-1}G \qquad (6)$$

Equation (6) is an attempt to extend the equation (4) of Argaman and Kaufman, which assumes a bimodal floc size distribution with a constant floc volume fraction, to a more generally applicable form.

Research on floc strength (Leentvaar (1982)) showed that after 20 to 30 minutes of flocculation the perimeter of the floc (P) was more or less constant.

With the assumption that P is constant, integration of equation (6) leads to

$$\Omega = \frac{bCe^{bt}}{1-aZe^{bt}} \qquad (7)$$

where

$a =$ $-C_FV^{-1}G$ (s^{-1})

$b =$ $C_FKV^{-1}G - C_BP^{-1}G$ (s^{-1})

$Z =$ integration constant

Equation (7) implies that at t is infinite a constant number of primary particles will remain unflocculated. The floc volume fraction at this time will be

$$-\frac{b}{a}\,.$$

CONCLUSION

The expression (6) is valid for a batch reactor. It could also be applied for a plug flow reactor; in that case t should be replaced by the mean residence time. Especially in such reactors it could be important to use an expression where the floc volume fraction is not assumed constant.

The appropriateness of equation (6) should be checked in experiments.

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5. EFFECT OF MAGNESIUM AND CALCIUM PRECIPITATION ON COAGULATION-FLOCCULATION WITH LIME

J. Leentvaar[1] and M. Rebhun[2]

1. Min. of Transport and Public Works, Delta Department, Env. Res. Sec., P.O. Box 439, Middelburg, the Netherlands.
2. Division of Environmental and Water Resources Engineering, Technion-Israel Institue of Technology, Haifa, Israel.

Abstract - Coagulation-flocculation studies were carried out to identify and quantify the organic matter (TOC) fraction removed by $Mg(OH)_2$ precipitation and the fraction removed due to $CaCO_3$ precipitation in lime treatment of wastewater. Most experiments were carried out with domestic sewage and some with a tannic acid solution simulating coagulable organics in wastewater. The experiments showed a clear relation between the amount of TOC removed and the amount of $Mg(OH)_2$ formed. This relation between TOC removal and $Mg(OH)_2$ precipitation can be expressed in terms of an adsorption isotherm.

The coagulation-flocculation tests of sewage with lime as a coagulant indicated that about 26% of the removable TOC in sewage is eliminated by $Mg(OH)_2$.

INTRODUCTION

Chemical treatment is applied in advanced treatment and renovation systems and lime is often used as a coagulant. Several authors have indicated the role of magnesium hydroxide as a coagulant aid in lime treatment.

Flentje (1927) reported an increase in clarification efficiency when excess lime was used to precipitate the magnesium in the water. Lecompte (1966) patented a process for using magnesium carbonate as a coagulant. Black and Christman (1961) showed that Mg^{2+} ions are adsorbed on the surface of the $CaCO_3$ particles at pH 9.8, thereby lowering or reversing the zeta potentials and corresponding mobility values. Van Vuuren et al (1967) described the role of magnesium hydroxide in lime softening and found that the structure of the $Mg(OH)_2$ floc was most suitable to adsorb $CaCO_3$, which normally tends to remain in suspension. The concluded that 1) the characteristically high magnesium content of their sewage effluent (ca. 100 mg l^{-1} Mg) due to the dolometic origin of their water supply appeared to be an important factor in lime flocculation/flotation and that 2) it seems that the use of dolometic lime as a coagulant might have inherent advantages for this purpose. Folkman and Wachs (1973) reported on experiments on algae removal from oxidation pond effluents by lime treatment and showed that magnesium hydroxide precipitation was responsible for flocculation of the algae.

Significant magnesium hydroxide precipitation can be expected at pH values greater than 10.5, due to its solubility constant. Such pH values are achieved at high lime treatment. However, low lime treatment is sometimes used, resulting in final pH values below 10.5 with little or no magnesium precipitation, calcium carbonate and phosphate being the main precipitation products. Significant reduction in suspended solids, extinction (light absorbing matter) and T.O.C. can be obtained by low lime treatment, however, much better clarity and lower TOC's are obtained at high lime treatment. Apparently, both calcium carbonate and magnesium hydroxide play a role in coagulation-flocculation with lime. Both calcium carbonate and magnesium hydroxide precipitated in lime treatment effect removal of suspended solids and TOC, magnesium hydroxide being able to flocculate and remove TOC fractions not affected by calcium carbonate alone.

The aim to this study was: a) to elucidate the role of magnesium precipitation in TOC removal and reduction of extinction, b) to quantify the TOC fraction that can be removed by calcium carbonate precipitation (low lime treatment) and the TOC fraction that can be removed only by coagulation-flocculation with magnesium hydroxide, c) to find a quantitative relationship between the amount of magnesium hydroxide and TOC removed.

PROGRAM OF STUDIES

To meet the research objectives, the experimental program included:

1. treatment at lime doses and final pH's where only calcium carbonate precipitates.
2. treatment at initial magnesium concentrations, lime doses and final pH's where various amounts of magnesium hydroxide would precipitate in addi-

tion to calcium carbonate. Addition of magnesium chloride to wastewater containing little magnesium was planned accordingly. To find quantitative correlations, various amounts of magnesium hydroxide were precipitated. This was accomplished in two different ways, either by a) optional addition of Mg to reach a constant high initial magnesium concentration and varying the lime dose and final pH, or by b) working at a constant final high pH and varying the initial magnesium concentration.

Both methods were used and a wide range of precipitated magnesium hydroxide was obtained and correlated with the reduction in TOC and extinction. The possible effect of final pH as a separate variable (not only through its effect on the amount of magnesium hydroxide) could be taken into account. Tannic acid solution was selected to represent organics that are removed by coagulation-flocculation and to investigate the mechanism and stoichiometry of the process in a controlled system.

EXPERIMENTS

The experiments were carried out with raw unsettled sewage from the village of Bennekom, Netherlands, mainly of domestic origin. This wastewater is of medium strength, as COD was about 500 mg $l^{-1}O_2$, BOD_5 was about 200 mg $l^{-1}O_2$ and TOC was about 170 mg $l^{-1}C$. The initial average magnesium concentration of the sewage amounted to 7 mg $l^{-1}Mg$. See Table 1.
In experiments where pH was varied, 80 mg $l^{-1}Mg$ was added to the sewage.

Table 1. Typical characteristics of the raw sewage

BOD_5	(mg $l^{-1}O_2$)	200
TOC	(mg $l^{-1}C$)	170
COD	(mg $l^{-1}O_2$)	500
Suspended solids	(mg l^{-1})	370
Extinction		0.4
pH		7.3
Alkalinity	(meq $l^{-1}HCO_3^-$)	7.00
Calcium	(mg $l^{-1}Ca^{2+}$)	34.5
Magnesium	(mg $l^{-1}Mg^{2+}$)	7.0
Spec.conductivity	(µS cm^{-1})	1100
Ortho-P	(mg l^{-1} P)	16
Total-P	(mg l^{-1} P)	23
Kjeldahl-N	(mg l^{-1} N)	90

Lime was used as a coagulant to obtain different pH values.

In experiments at constant final pH various amounts of magnesium chloride were added to obtain initial concentrations ranging from 5 to 44 mg l^{-1}Mg. Lime was dosed to a final pH of 11.5.

The experiments with simulated organics were carried out with a solution of tannic acid in distilled water at concentrations of 40, 80 and 100 mg l^{-1} and with four different initial magnesium chloride concentrations: 12.1, 22.1, 32.1, 42.1 mg l^{-1}Mg. Two litre samples were coagulated-flocculated at different pH's (8.8, 9.5, 10.5 and 11.5). NaOH was used to raise the pH to the desired value. The batch coagulation-flocculation tests were done in rectangular 2 litre plexiglass tanks with a cross-sectional area of 10 x 10 cm^2. The following experimental procedures were used:

1. Mixing with a turbine type stirrer at 660 rev min^{-1}, which gave a mean G value of 680 s^{-1}.
2. Addition of coagulant and adjustment of pH over a 60 s period at 660 rev min^{-1} (rapid mix).
3. Flocculation for 30 min with a propeller type stirrer at 90 rev min^{-1} (G = 41 s^{-1}).
4. Sedimentation for 30 minutes.

The G value was measured with a pilot scale dynamometer as described by Leentvaar and Ywema (1980).

After sedimentation, a sample of about 100 ml was withdrawn at half height of the tank and the following parameters were determined: Extinction at 620 nm wavelength in a cuvette (diameter = 2 cm), TOC, Mg^{2+} and Ca^{2+} concentrations. In case of tannic acid solution, TOC and Mg^{2+} concentration were determined.

RESULTS

In the experiments carried out with Bennekom sewage with lime as a coagulant and an initial magenesium concentration in the wastewater of 7 mg l^{-1} Mg or 80 mg l^{-1}Mg, the reduction of extinction (E) and TOC were measured at different pH values obtained by different lime doses as illustrated in Fig. 1. These experiments showed that for the same effect a higher pH was required in case of a low initial Mg concentration in the sewage as compared to a high Mg concentration.

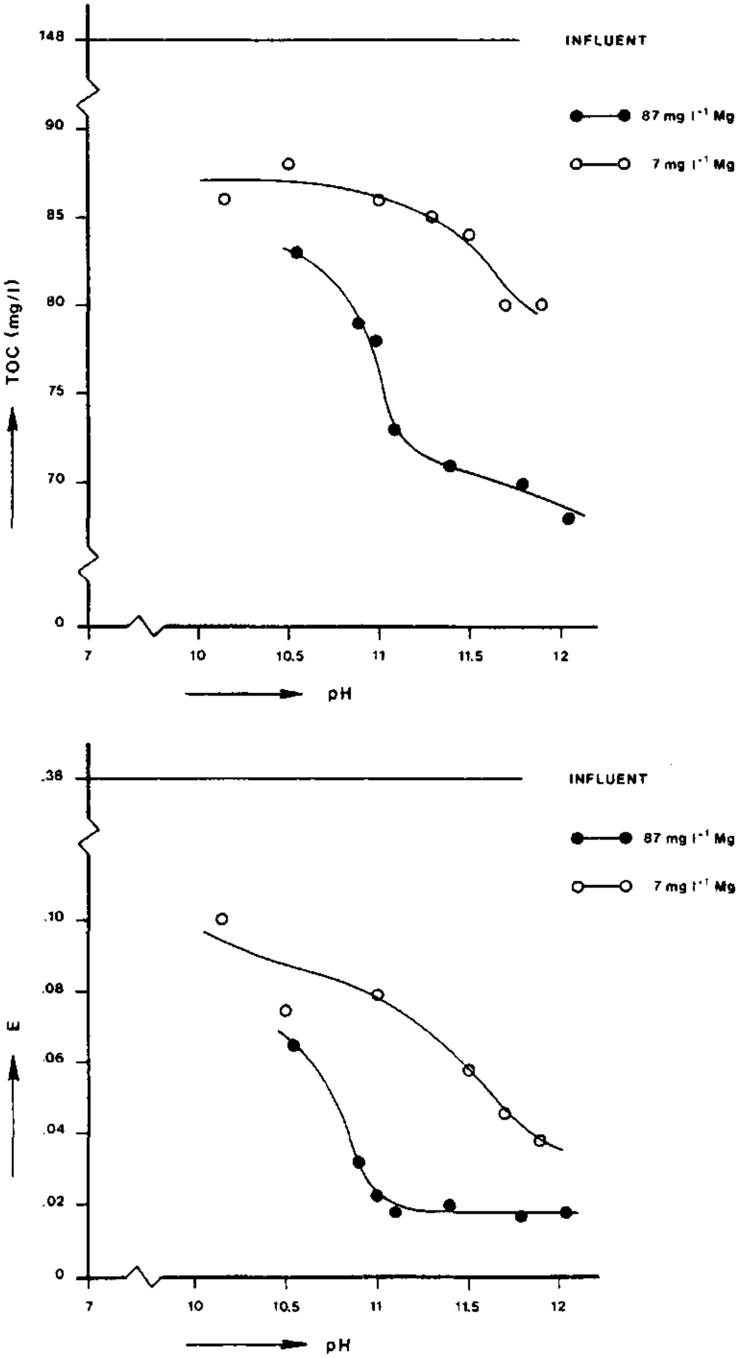

Fig. 1. Wastewater flocculated at different pH values with lime as coagulant and with 87 mg l^{-1}Mg and with 7 mg l^{-1}Mg as initial magnesium concentration.

This is due to the different amounts of precipitated magnesium hydroxide - the compound responsible for reducing the colloidal TOC fraction and extinction. The precipitation of $Mg(OH)_2$ was found to be inhibited in wastewater, as can be seen in Fig. 2 where residual Mg calculated from the solubility constant is compared with Mg residuals actually obtained in the experiments.

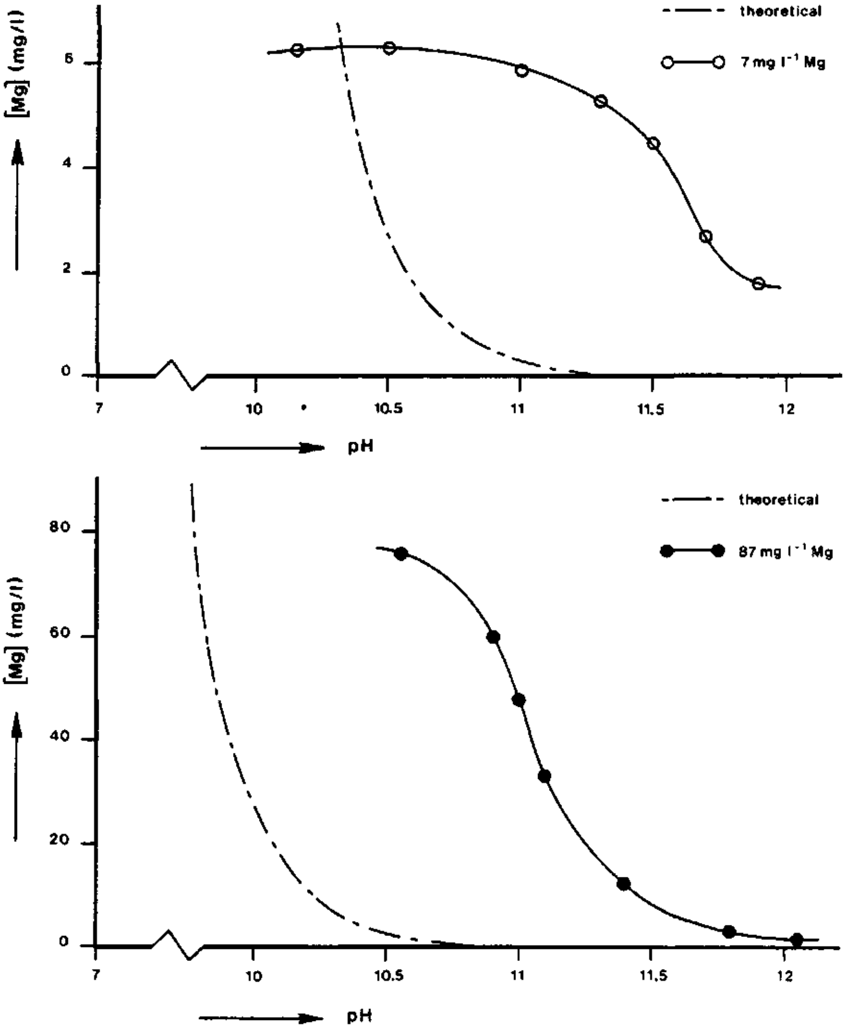

Fig. 2. Wastewater flocculated at different pH values. The inhibition of the $Mg(OH)_2$ precipitation is illustrated by the theoretical line and the measured magnesium concentration with a high and a low initial concentration of Mg^{2+}.

It should be noted that a large fraction of TOC is removed and a high reduction in extinction is obtained below the insolubilization pH of $Mg(OH)_2$. This is due to plain settling of the settleable fractions as well as to settling of dispersed matter aided by the precipitation of $CaCO_3$. The reduction of TOC from 148 mg/l to 85 mg/l shown in Fig. 1 is due to this mechanism. Any further reduction in TOC below 85 mg/l could be achieved only through $Mg(OH)_2$ precipitation.

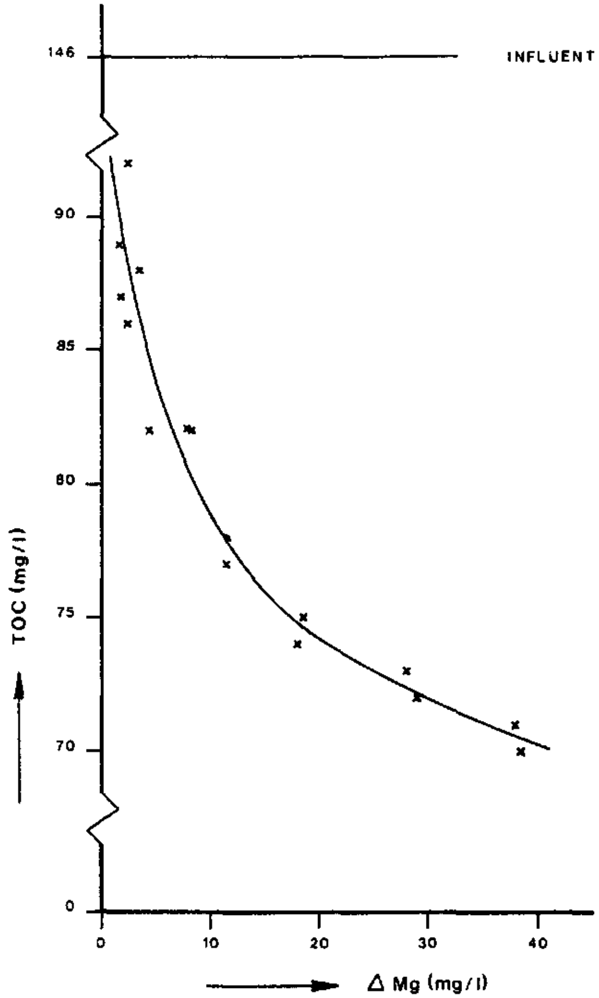

Fig. 3. Sewage flocculated at pH 11.5 with lime with different initial Mg concentrations.

Another series of coagulation-flocculation experiments with lime as a coagulant were carried out at a constant pH, higher than 10.5 and a variable addition of magnesium chloride to the sewage in order to obtain various amounts of magnesium precipitates (ΔMg), so as to be able to correlate TOC and extinction reduction to the precipitated amount of $Mg(OH)_2$. By these experiments the stoichiometric, quantitative relationships between the amount of TOC (ΔTOC) or extinction (Δextinction) removed and the amount of magnesium hydroxide formed could be evaluated. An illustration of results of the coagulation-flocculation experiments with lime as a coagulant at variable initial Mg concentrations and fixed pH of 11.5 is given in Fig. 3 and Fig. 4 where TOC and E are plotted versus ΔMg.

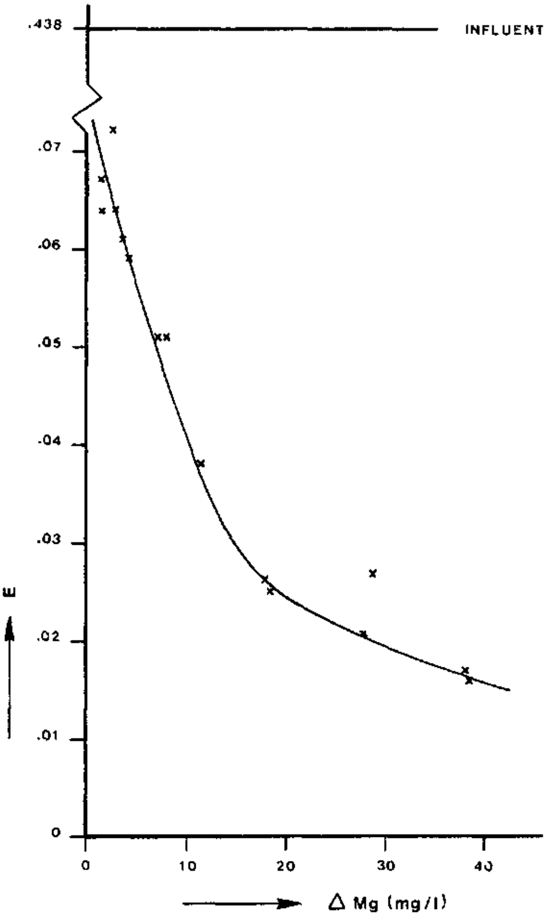

Fig. 4. Sewage flocculated at pH 11.5 with lime with different initial Mg concentrations.

It can also be seen in these figures that a large reduction in TOC (from 146 mg/l to 90 mg/l) and extinction (from 0.438 to 0.07) was obtained without any significant Mg precipitation. But reductions below these values could be accomplished only by precipitation of Mg $(OH)_2$ and residual concentrations of TOC decreased with increase of ΔMg.

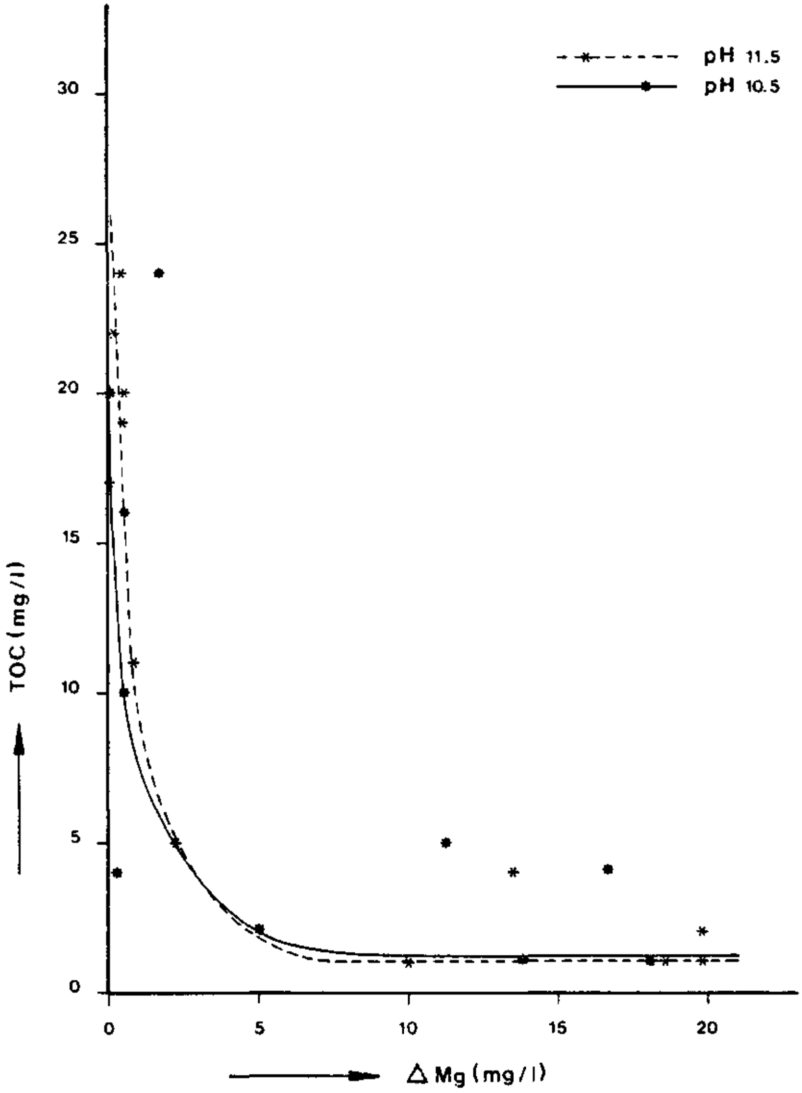

Fig. 5. Tannic acid solution flocculated at pH 10.5 and pH 11.5 with different initial Mg and tannic acid concentrations.

Results of flocculation experiments with tannic acid at various Mg concentrations at pH 10.5 and 11.5 are shown in Fig. 5. In this case removal is due only to precipitated $Mg(OH)_2$ since no other components except Mg and tannic acid were present. Experiments at pH 8.8 and 9.5, which are below Mg insolubilization, showed no tannic acid removals, except at very high Mg concentrations, where some removal was perceptible, possibly by Mg-tannate formation.

DISCUSSION

Many research workers reported that the residual concentration of TOC and extinction decreased as the amount of magnesium removed during lime coagulation-flocculation increased (Minton and Carlson (1973), Mennel et al (1974), van Vuuren et al (1967)).

It has been observed (Berg et al (1970)), with both raw wastewater and secondary effluent, that clarification occurred at an insolubilization pH of only 9.5 in high hardness/high alkalinity wastewater. In contrast the treatment of low hardness/low alkalinity wastewaters has required a pH of 11.0 to 11.5 for satisfactory clarification and in many instances a coagulant aid such as ferric chloride or an organic polymer has been required (Wuhrman, (1968)).

The results of the work described in the present paper are in agreement with and explain the various findings cited above. In lime treatment of wastewater both $CaCO_3$ and $Mg(OH)_2$ are effective in the flocculation-clarification and removal processes:

1. The precipitated $CaCO_3$ acts by the "sweep coagulation" mechanism affecting the removal of suspended solids and easily coagulable large colloidal material. It also aids in settling as a "weighting agent" by increasing the density of the settling aggregates. However, stable and organic colloids cannot be affected by calcium carbonate.

   Significant amounts of $CaCO_3$ precipitation can be obtained in high alkalinity (bicarbonate) waters.
2. The precipitating $Mg(OH)_2$ acts by an adsorptive coagulative mechanism. Its structure which provides a large adsorptive surface area and its positive electrostatic surface charge enables it to act as a powerful and efficient coagulant also on stable organic colloids and give high degrees of clarification.

Significant amounts of $Mg(OH)_2$ can be expected at high lime doses giving high pH's and in waters containing sufficient Mg.

In order to separate quantitatively the effect of $Mg(OH)_2$ formation from the effect of $CaCO_3$ precipitation the fraction of TOC and extinction removed by calcium carbonate alone (ΔC_{Ca}) has to be estimated.

This can be done by two methods:

1. Based on the plot of TOC or extinction versus pH, extrapolation to a lower pH (see Fig. 1), where there is no $Mg(OH)_2$ precipitation (below pH 10.0 according to Fig. 2).
2. Based on a plot of TOC or extinction versus ΔMg, extrapolation to $\Delta Mg = 0$ (which means no $Mg(OH)_2$ precipitation).

This second method was selected to determine the amount of TOC or extinction removed by calcium carbonate alone. This method is illustrated in Fig. 6. The experiments with sewage showed that on average 45% of TOC and 85% of extinction was removed with the aid of $CaCO_3$.

The determination of the amount of non-removable (soluble) TOC or extinction (C_{NR}) by both calcium carbonate and magnesium hydroxide was done by determination of the asymptotic value of the TOC or extinction to the curve of TOC or extinction versus ΔMg at high ΔMg, which is equivalent to a large amount of $Mg(OH)_2$ precipitated. This also is illustrated in Fig. 6.

On average the non-removable portion of TOC or extinction by lime coagulation-flocculation of sewage amounted to 39% and 8% respectively.

The evaluation of the adsorption capacity of $Mg(OH)_2$ was based on the assumption that magnesium hydroxide removes only magnesium removable TOC. In order to evaluate the adsorption capacity of $Mg(OH)_2$ the following parameters were defined (see Fig. 6):

C_0: TOC of raw sewage

C_R: Total residual TOC after coagulation-flocculation and settling

C_{Ca}: Residual TOC after lime treatment at high pH at ΔMg is equal to 0

C_{NR}: Non-removable residual TOC = asymptotic value of C_R at high ΔMg

C_{Mg}: Residual Mg removable TOC = $C_R - C_{NR}$

ΔC_{Ca}: Amount of TOC removed by $CaCO_3$ precipitation alone = $C_0 - C_{Ca}$

ΔC_{Mg}: Amount of TOC removed by $Mg(OH)_2$-floc = $C_{Ca} - C_R$

ΔMg: Amount of magnesium precipitated = initial-residual magnesium concentration

From the data of the experiments carried out at pH values higher than 10.5 the amount adsorbed (ΔC_{Mg}) per unit adsorbent $Mg(OH)_2$ (expressed as Δ Mg) was calculated at constant pH. This value $\Delta C_{Mg}/\Delta Mg$ is related to the concentration of adsorbate remaining in solution (C_{Mg}). An example of this calculation is given in Table 2.

Adsorption isotherms, as illustrated by Fig. 7 through Fig. 9, show that in case of sewage the maximal adsorption capacity ranges from 1.5 to 3.0 mg TOC/mg Mg, independent of wastewater composition, TOC ranging from 140 to 220 mg l^{-1}C and independent of pH. The wastewater samples were taken in

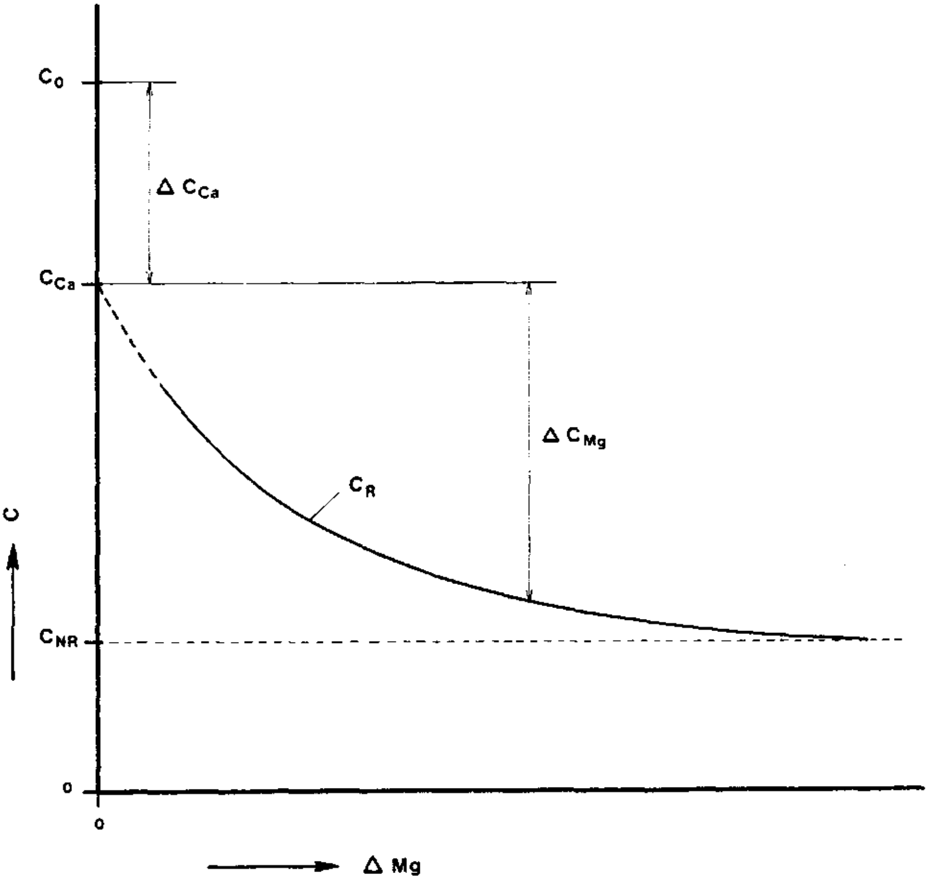

Fig. 6. Illustration of the method used to determine the amount of TOC removed by calcium carbonate (ΔC_{Ca}), the amount removed by $Mg(OH)_2$ precipitation (ΔC_{Mg}) and the non-removable fraction of TOC (C_{NR}).

a span of two months. The removal of organic substances by adsorption by $Mg(OH)_2$ shows a behaviour similar to an adsorption isotherm and fits in a Freundlich equation with a correlation coefficient (r) ranging from 0.81 to 0.91. This value r is significant with a significance level of 0.01.

The removal of tannic acid by adsorption coagulation on $Mg(OH)_2$ also shows a behaviour similar to a Freundlich adsorption isotherm at pH 10.5 and pH 11.5 at which $Mg(OH)_2$ precipitated (r = 0.85 and 0.92 respectively). The removal of tannic acid at pH 8.8 and 9.5 where no $Mg(OH)_2$ precipitates shows no similarity with a Freundlich adsorption isotherm (r = 0.51 and 0.28 respectively).
The adsorption isotherms of the tannic acid on $Mg(OH)_2$ at pH greater than 10.5 show a maximal adsorption capacity of about 13 mg TOC/mg Mg as illustrated in Fig. 10. The adsorption capacity for tannic acid is about four times higher than that for organics in sewage. This is possibly due to the different nature of the specific compounds involved, as well as to the fact that in sewage treatment part of the $Mg(OH)_2$ is used for flocculation of ΔC_{Ca}.

Table 2. Example of the calculation of the adsorption capacity of TOC on $Mg(OH)_2$ floc in lime treatment of sewage. Data from Fig. 3. $C_0 = 146$ mg $l^{-1}C$, $C_{Ca} = 95$ mg $l^{-1}C$, $C_{NR} = 68$ mg $l^{-1}C$.

C_R (mg $l^{-1}C$)	ΔC_{Mg} (mg $l^{-1}C$)	Mg_0 (mg $l^{-1}Mg$)	Mg_R (mg $l^{-1}Mg$)	ΔMg (mg $l^{-1}Mg$)	$\Delta C_{Mg}/\Delta Mg$ (mg C/mg Mg)	C_{Mg} (mg $l^{-1}C$)
89	6	5.4	3.8	1.6	3.75	21
87	8	5.4	3.7	1.7	4.71	19
92	3	7.2	4.8	2.4	1.25	24
86	9	7.0	4.7	2.3	3.91	18
88	7	9.0	5.6	3.4	2.06	20
82	13	9.1	4.8	4.3	3.02	14
82	13	13.1	5.2	7.9	1.65	14
82	13	12.9	5.6	7.3	1.78	14
78	17	16.6	5.2	11.4	1.49	10
77	18	16.6	5.2	11.4	1.58	9
75	20	24.2	5.8	18.4	1.09	7
74	21	24.2	6.1	18.1	1.16	6
73	22	34.2	6.1	28.1	0.78	5
72	23	34.4	5.6	28.8	0.80	4
71	24	44.0	5.9	38.1	0.63	3
70	25	44.0	5.4	38.6	0.65	2

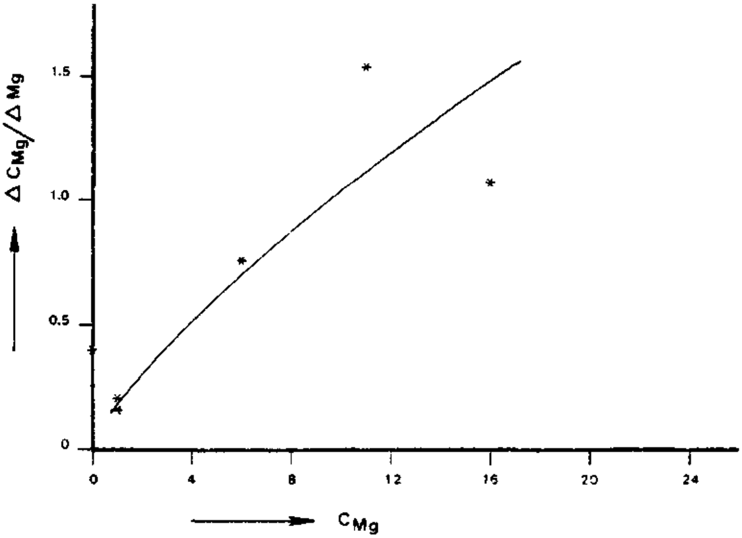

Fig. 7. The amount of TOC removed by $Mg(OH)_2$ precipitation divided by amount of magnesium removed plotted versus the residual magnesium removable TOC in terms of an adsorption isotherm in case of sewage.

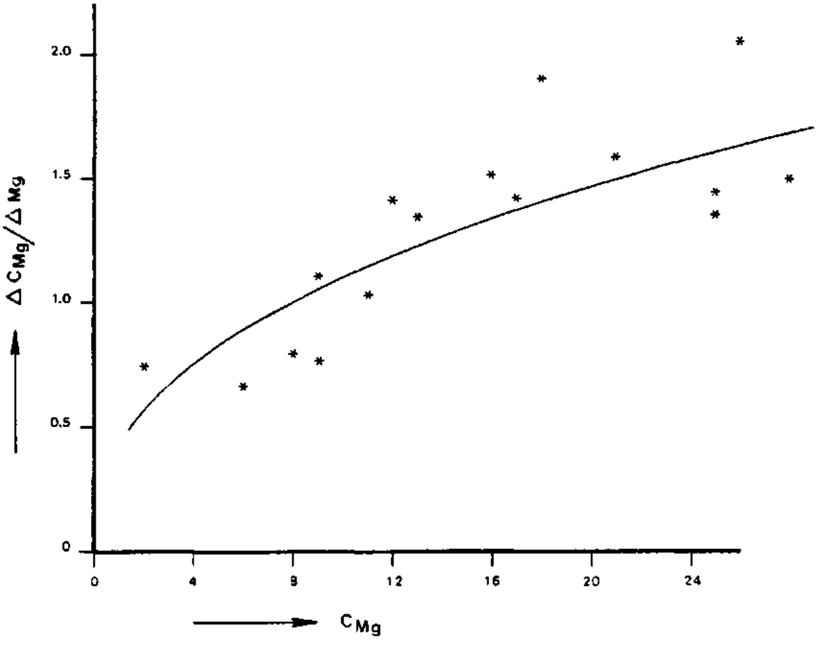

Fig. 8. The amount of TOC removed by $Mg(OH)_2$ pricipitation divided by amount of magnesium removed plotted versus the residual magnesium removable TOC in terms of an adsorption isotherm in case of sewage.

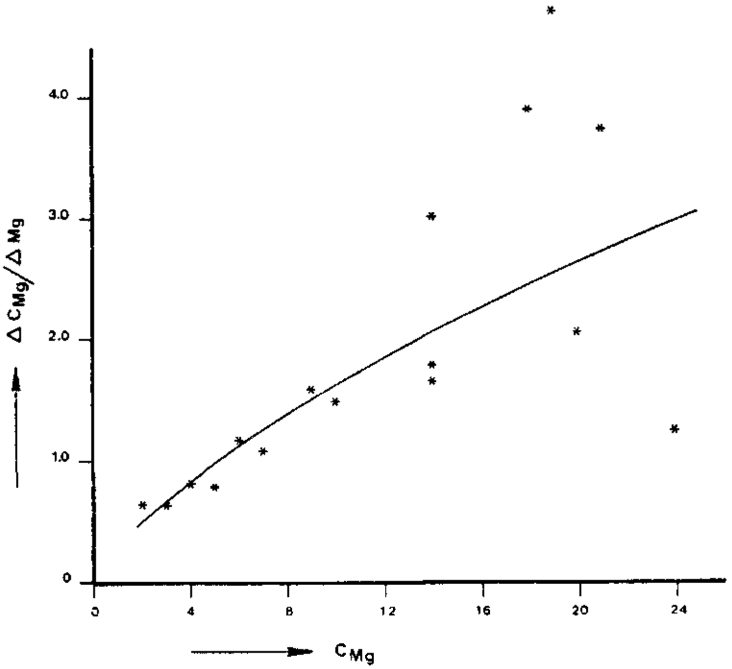

Fig. 9. The amount of TOC removed by $Mg(OH)_2$ precipitation divided by amount of magnesium removed plotted versus the residual magnesium removable TOC in terms of an adsorption isotherm in case of sewage.

CONCLUSION

The study has shown that two major mechanisms are effective in lime coagulation-flocculation of sewage:

1. Sweep coagulation by $CaCO_3$
2. Adsorption-coagulation of stable organic colloids by $Mg(OH)_2$.

The last mechanism provides high clarity effluents.

The experiments with sewage showed that on an average:

- 45% of TOC and 85% of extinction could be removed by $CaCO_3$ formation;
- an additional 16% of TOC and 7% of extinction of the raw sewage could be removed by $Mg(OH)_2$ precipitation;
- the non-removable fraction amounted to about 39% of TOC and 8% of extinction.

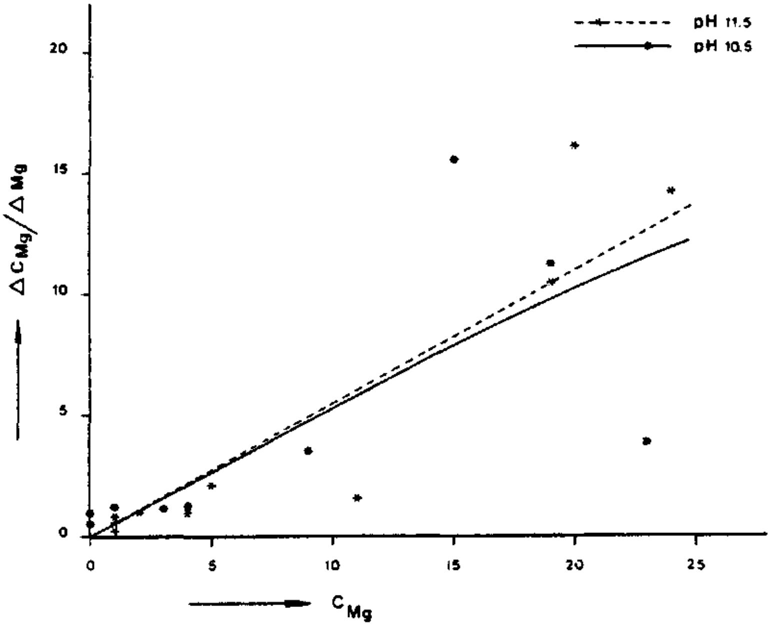

Fig. 10. The amount of TOC removed by $Mg(OH)_2$ precipitation divided by amount of magnesium removed plotted versus the residual magnesium removable TOC in case of a tannic acid solution.

The relation between removal of TOC or extinction and $Mg(OH)_2$ precipitation expressed as an adsorption isotherm showed a behaviour similar to that of an adsorption process. The maximal adsorption capacity varied between 1.5 to 3.0 mg TOC/mg Mg for different sewage samples and amounted to 13 mg TOC/mg Mg for a tannic acid solution.

Although the curves are similar to a Freundlich adsorption isotherm, this does not prove that adsorption is the only process involved.

In practice, coagulation-flocculation with lime should give better removals with a high initial magnesium content in the water. In case of a low magnesium content of the water treatment with lime which contains magnesium is to be preferred.

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6. OPTIMALIZATION OF COAGULANT DOSE IN COAGULATION-FLOCCULATION OF SEWAGE

J. Leentvaar, T. S. J. Ywema and R. E. Roersma
Department of Water Purification, Agricultural University, Wageningen, The Netherlands

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Abstract— This article describes how the optimal coagulant dose in chemical treatment can be calculated from a limited number of raw sewage characteristics. Ferric chloride and aluminium sulphate were used as coagulants. In jar tests ten characteristics were determined in the sewage and for each separate sample of wastewater "optimal" coagulant doses were determined. There was a very high correlation between the "optimal" dose of aluminium sulphate and ferric chloride and one or two quality parameters of the influent. A comparison was made between aluminium sulphate and ferric chloride as coagulant. The findings were verified in two pilot plants. In one a constant coagulant dose m^{-3} influent was set; in the other plant the coagulant dose was also related to the orthophosphate content of the sewage. By this means a reduction of the coagulant dose was obtained of 35%, while on average the removal percentage of TOC was the same.

INTRODUCTION

Though the capital cost of a physico-chemical wastewater treatment plant is lower than those of a mechanical–biological plant, its recurring costs are mostly higher. The costs that mainly recur are those for the coagulants. In practice the optimal coagulant dose is established by jar tests and a constant dose m^{-3} influent is set. Thus if the plant is connected to a combined sewerage system, where rainfall causes a higher flow of wastewater, the coagulant dose per time is increased. Often it is uncertain whether this increase is necessary for the removal of organic material. It is of great importance to gain more understanding about the optimal coagulant dose in relation to characteristics of the sewage. These parameters should be easy to determine automatically.

Information on any relation between optimal coagulant dose and sewage parameters can provide insight into the nature of the coagulation–flocculation process. Therefore different samples of the wastewater of the village Bennekom, which is mainly of domestic origin, were tested. This village has a combined sewerage system.

EXPERIMENTAL PROCEDURES

The experiments were carried out with raw unsettled sewage of medium strength as COD was about 433 mg $O_2 l^{-1}$, BOD_5 was about 171 mg $O_2 l^{-1}$ and TOC was about 140 mg C l^{-1}. Wastewater samples of 50 l. were taken at different times of the day under different weather conditions. The study was confined to 21 samples. To determine the optimal coagulant dose, with each sample of sewage a series of 24 batch experiments were carried out with an increasing dose of ferric chloride or aluminium sulphate. Ten parameters of the sewage were determined: pH, alkalinity, specific conductivity, transmission, content of suspended solids, of total organic carbon (TOC), of dissolved organic carbon (DOC), amount of orthophosphate, of total phosphorus and of Kjeldahl nitrogen. The alkalinity was determined automatically with an autotitrator by titration to pH 4.1.The transmission was determined at 620 nm wavelength and with a cuvette diameter of 2 cm. The DOC value in our investigation was defined as the content of organic carbon in the sample after filtration through a 0.45 μm membrane. The other analyses and measurements were made according to *Standard Methods* (1971). Immediately after sampling, the tests were carried out, so that the temperature did not undergo any change during the test. The results of the measurements and analyses of the 21 samples are summarized in Table 1.

The coagulation flocculation tests were done in rectangular 2 l. Plexiglas tanks with a cross area of $10 \times 10\,cm^2$. The test procedure was as follows:

1. Mixing with a turbine type stirrer at 660 rev min^{-1}, which gave a G value of $680\,s^{-1}$
2. Coagulant dose in solid form and pH-adjustment for 60 s at 660 rev min^{-1}.
3. Flocculation for 30 min with a propeller type stirrer at 67 rev min^{-1} ($G = 28\,s^{-1}$).
4. Sedimentation for 30 min.

After sedimentation, a sample was taken at half height of the tank. The G value was measured with a torque meter. The test conditions such as mixing time and mixing intensity were kept constant during all experiments. For coagulation–flocculation was the pH adjusted to 5.3 with ferric chloride and to 5.5 with aluminium sulphate as coagulant. These pH values were shown to be the optimum pH values for the chemical treatment of the sewage of Bennekom (Leentvaar *et al.*, 1978). In the supernatant, four parameters were determined: the transmission (T) (wavelength 620 nm, cuvette diameter 2 cm), the content of TOC and the concentration of total phosphorus and orthophosphate. A typical example is shown in Figs. 1 and 2 for ferric chloride and aluminium sulphate coagulation–flocculation respectively. To determine whether it is necessary or not to measure four characteristics in the supernatant, the correlation coefficient (r) was calculated between the transmission and the total phosphorus content and between the transmission and the TOC of the supernatant of a series of experiments. This was done for the first eight series. The average correlation coefficients (r) are shown in Table 2.

From Figs. 1 and 2 and Table 2 it can be concluded there is an exceptional high correlation between transmission and TOC, and between transmission and total phos-

Table 1. Composition of the 21 sewage samples examined

	Average	Standard deviation	Range
pH	7.25	0.47	6.20–7.90
Alkalinity (meq HCO_3^- l^{-1})	7.02	2.03	2.40–9.92
Spec. conductivity (μS cm^{-1})	1085	300	425–1450
Transmission (%)	31	16	5–54
Suspended solids (mg l^{-1})	369	83	2–3390
TOC (mg C l^{-1})	219	93	84–453
DOC (mg C l^{-1})	73	28	45–150
Ortho-P (mg P l^{-1})	16	5.2	4.3–28
Total-P (mg P l^{-1})	23	9.2	6.6–41
Kjeldahl N (mg N l^{-1})	89	33	34–170
Temperature (°C)			15–17

phorus content in the supernatant, so that in future the value of the transmission can be used to determine the "optimal" coagulant dose, also with regard to phosphorus and TOC removal.

Overath & Marr (1976) defined the optimal coagulant dose as the amount of coagulant where the tangent to the curve "coagulant dose vs transmission" at the point of inflexion intersects the line, asymptotic to the maximal transmission percentage (see Fig. 3). The asymptote to the maximal transmission value turned out to be horizontal in all experiments. The "inflexion point optimal dose" is mentioned here as y_1. However, it is difficult to determine the tangent to the curve at the point of inflexion accurately.

In our paper, another way of defining the optimal coagulant dose was also applied, in determining that amount of coagulant to meet 90% of the maximal transmission value (see Fig. 4). The "90% optimal dose" is mentioned as y_2.

Besides the optimal coagulant dose Overath & Marr (1976) determined a critical coagulant dose: below this dose no coagulation-flocculation effect was measurable (see Fig. 3). In our experiments the curve "transmission vs coagulant dose" was always the same shape as the one in Fig. 4.

So in the experiments with the sewage of Bennekom, it was not well possible to determine a critical coagulant dose, because already at a coagulant dose less than 0.01 mmol l^{-1} of Fe and Al a change in transmission, TOC and phosphorus content of the supernatant was perceptible.

RESULTS

Results of the first eight treated samples of sewage show that the optimal coagulant dose y_1 corresponded to 40.5 and 43.2% TOC-removal for ferric chloride and aluminium sulphate as coagulant respectively; the optimal coagulant dose y_2 involves 51.7 and 52.1% TOC-removal respectively. The maximal removal of TOC in these eight experiments was on average 59.1% with ferric chloride and 57.4% with aluminium sulphate as coagulant. The determination of optimal coagulant doses y_1 and y_2 was based on the transmission. The "inflexion point optimal value" (y_1) corresponded to about 72% of the maximal TOC-removal and the "90% optimal coagulant dose" (y_2) corresponded to about 89% of the maximal TOC-removal.

The total phosphorus removal showed similar values. The optimal coagulant dose y_1 corresponded to 67.0 and 72.1% P-removal for ferric chloride and aluminium sulphate as coagulant respectively; the

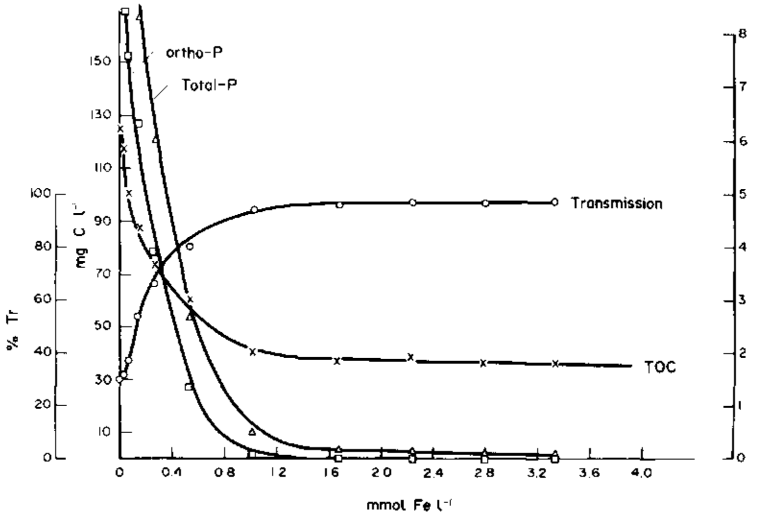

Fig. 1. A typical result of a coagulation–flocculation test with ferric chloride as coagulant.

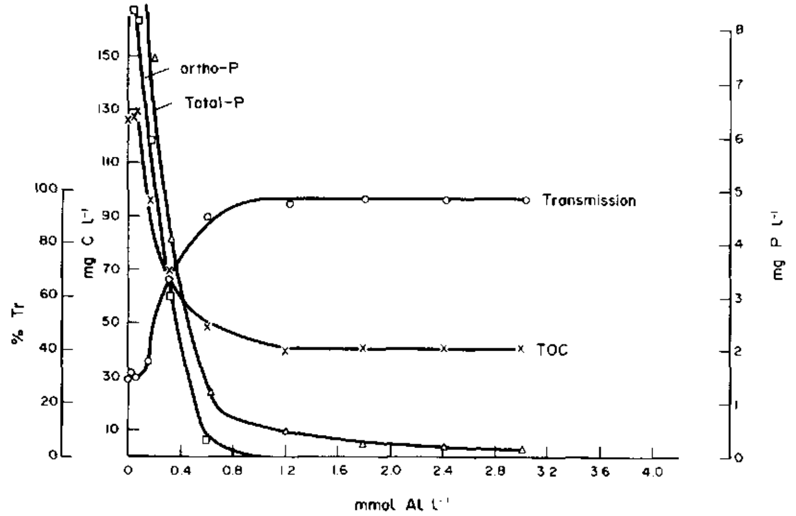

Fig. 2. A typical result of a coagulation-flocculation test with aluminium sulphate as coagulant.

Table 2. Average correlation coefficients (r) between transmission (T) and total phosphorus concentration and between transmission and TOC of the supernatant in the first eight series of experiments

Coagulant	r(T-total-P)	r(T-TOC)
$FeCl_3 \cdot 6H_2O$	0.99	0.96
$Al_2(SO_4)_3 \cdot 18H_2O$	0.99	0.97

optimal coagulant dose y_2 involved 91.1 and 89.8% P-removal respectively. The maximal percentage removal of phosphorus was on average 98.8% with ferric chloride and 97.9% with aluminium sulphate as coagulant. For the "inflexion point optimal value" (y_1), these values corresponded to about 71% and for the "90% optimal value" (y_2) to about 92% of the maximal P-removal. In most experiments, the optimal dose y_1 was less than the coagulant dose y_2 for both coagulants.

Table 3 presents simple correlation coefficients (r) between the parameters of the raw sewage.

A very high correlation was found between the alkalinity and the specific conductivity of the sewage (0.963), which seems to be quite normal. As the alkalinity of the drinking water of Bennekom is relatively low, 1.41 meq. HCO_3^- l⁻¹, the phosphate concentration could play a role of importance in relation to the total alkalinity of the sewage. From the dissociation constants for the acidbase reactions in water of H_3PO_4, $H_2PO_4^-$ and HPO_4^{2-}, it can be calculated that the reaction $HPO_4^{2-} + H^+ \leftrightharpoons H_2PO_4^-$ occurs during the determination of alkalinity. This phenomenon explains the relatively high correlation coefficient between the alkalinity and the orthophosphate

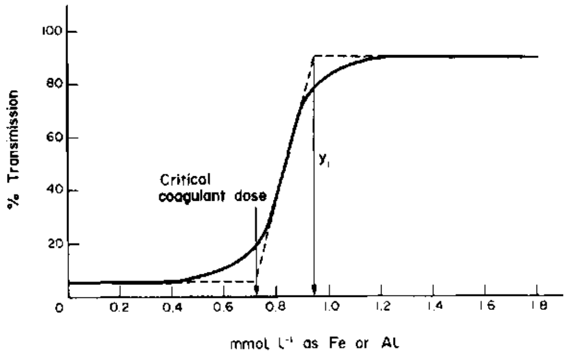

Fig. 3. Definition of the "inflexion point optimal coagulant dose" (y_1) and the critical coagulant dose.

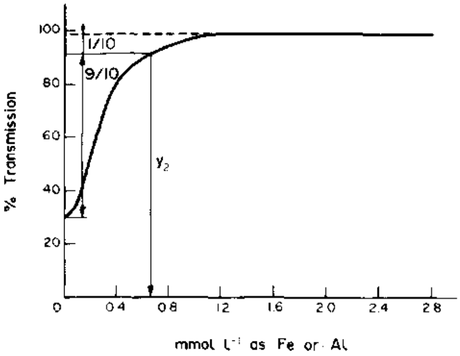

Fig. 4. Definition of the "90% optimal dose" (y_2).

content of the sewage (0.884). In the wastewater of Bennekom, 71% of the phosphorus is present as orthophosphate. There was also a high correlation between alkalinity and total phosphorus content (0.841).

Table 4 shows the simple correlation coefficients (r) between the "inflexion point optimal dose" (y_1), the "90% optimal coagulant dose" (y_2) and the raw sewage characteristics for both ferric chloride and aluminium sulphate as coagulant.

Table 4 shows that the correlation between almost all sewage parameters and the optimal dose y_1 was lower than the correlation between the sewage parameters and the optimal dose y_2. This difference may be caused by the difficulty of drawing accurately a tangent to the curve at the point of inflexion. Therefore this value y_1 is less accurate than the value y_2. Some reflections on these correlations are given:

1. The pH value.

All coagulation–flocculation experiments were carried out at a fixed pH (5.3 for ferric chloride and 5.5 for aluminium sulphate). Because of this fixed flocculation pH and the poor correlation between the pH and the other sewage parameters, there seems to be no reason for a very high correlation between sewage pH and optimal coagulant doses. Table 4 shows that the simple correlation coefficient between sewage pH and optimal coagulant doses ranged from −0.018 and 0.563. It is remarkable that the correlation between both "inflexion point optimal doses" and the pH value was much higher than with the "90% optimal coagulant dose".

2. The alkalinity.

The correlation coefficient between the alkalinity of the raw sewage and the optimal coagulant doses y_1 and y_2 with ferric chloride and aluminium sulphate was 0.625 on average. Table 3 shows a high correlation between alkalinity and the other sewage characteristics. The main component of the total alkalinity is the carbonate content, which is not in a strict sense part of the pollution and is not eliminated by coagulation. The relative high correlation with the ortho and total-P content has been mentioned already. Though the correlation between alkalinity and TOC or DOC was not so very high (0.556 and 0.429 on average respectively), it is surprising that the sewage alkalinity had such a high correlation with the optimal coagulant dose, which was determined from transmission, content of TOC and of P of the supernatant.

3. The specific conductivity.

A remarkable correlation was found between the specific conductivity and the optimal coagulant dose

Table 3. Simple correlation coefficients (r) between the sewage characteristics, as specified in Table 1

	pH	Alkalinity	Conductivity	Transmission	Suspended solids	TOC	DOC	Ortho-P	Total-P	Kjeldahl-N
pH	1.000									
Alkalinity	0.360	1.000								
Conductivity	0.387	0.963	1.000							
Transmission	0.136	−0.433	−0.301	1.000						
Suspended solids	−0.265	0.402	0.190	−0.610	1.000					
TOC	0.157	0.556	0.479	−0.790	0.345	1.000				
DOC	0.154	0.429	0.418	−0.249	0.156	0.674	1.000			
Ortho-P	0.046	0.884	0.853	−0.443	0.548	0.415	0.379	1.000		
Total-P	0.115	0.841	0.747	−0.643	0.663	0.578	0.356	0.880	1.000	
Kjeldahl-N	0.086	0.827	0.716	−0.613	0.774	0.549	0.352	0.866	0.863	1.000

Table 4. Simple correlation coefficients (r) between the optimal coagulant doses y_1 and y_2 and the sewage parameters for ferric chloride and aluminium sulphate

Coagulant (mmol l^{-1} Fe or Al):	$FeCl_3 \cdot 6H_2O$		$Al_2(SO_4)_3 \cdot 18H_2O$	
	y_1	y_2	y_1	y_2
pH	0.563	0.125	0.420	−0.018
Alkalinity (meq HCO_3^- l^{-1})	0.439	0.702	0.658	0.701
Spec. conductivity (μS cm^{-1})	0.470	0.652	0.666	0.616
Transmission (%)	−0.033	−0.461	−0·379	−0.689
Suspended solids (mg l^{-1})	0.534	0.221	0.663	0.766
TOC (mg C l^{-1})	0.055	0.351	0.359	0.420
DOC (mg C l^{-1})	0.075	0.200	0.152	0.092
Ortho-P (mg P l^{-1})	0.397	0.785	0.600	0.808
Total-P (mg P l^{-1})	0.551	0.981	0.726	0.899
Kjeldahl-N (mg N l^{-1})	0.285	0.710	0.608	0.831

(on average 0.601). An explanation for this phenomenon is difficult. The presence of for instance sulphate ions influences the coagulation–flocculation: these ions increase the optimal pH-range especially to lower pH-levels in both ferric chloride and aluminium sulphate systems [Hsu (1976) and Packham (1965)].

4. The transmission.

The transmission percentage of the sewage at 620 nm has a low correlation with the optimal coagulant dose (on average −0.391). As the turbidity of wastewater is difficult to determine, the transmission was used instead. For production of drinking-water, Conley & Evers (1968) recommended a coagulant control according to turbidity. Our study showed that the percentage transmission of the sewage tested is a poor parameter for coagulant control.

5. Content of suspended solids.

Suspended solids consist mainly of compounds which do not need any coagulation–flocculation in order to settle in the sedimentation tank. Hence it is evident that the content of suspended solids cannot be an adequate parameter for the coagulant dose; only when there is a correlation between content of suspended solids and some other parameter of the sewage can this content play a role of importance.

6. The total and dissolved organic carbon content (TOC and DOC).

In general there will be no high correlation between the optimal coagulant dose and the DOC content of the sewage, as is shown by the low correlation coefficient of 0.130. In the samples tested, the DOC was about one third of the TOC value. The content of TOC of the sewage did not show a high correlation with the optimal coagulant doses; the simple correlation coefficient ranged from 0.055 to 0.420. Tenny & Stumm (1965) found a linear relation between the required coagulant dose and the concentration of a bacterial suspension measured in terms of COD. Besides particles of colloidal character and suspended solids, the sewage contains a fraction of soluble compounds, which can all be measured in terms of TOC. Hence the TOC value cannot be a determinant factor for coagulant control.

7. The phosphorus content.

Table 4 shows that the highest correlation was between optimal coagulant dose and total phosphorus content of the sewage. The phosphorus was present in the sewage for about 29% as organic phosphorus compounds and as polyphosphates and for about 71% as orthophosphate. The correlation between the optimal coagulant dose and the ortho-P concentration in the sewage was also high (on average 0.648). The simple correlation coefficient between the total phosphorus content and the "90% optimal values" (y_2) was for both aluminium sulphate and ferric chloride about 0.9.

8. The Kjeldahl-nitrogen content.

The simple correlation coefficient between the sum of ammonium and organic nitrogen compounds in the sewage and the optimal coagulant doses was on average 0.609. The ammonium–N content was about one third of the total nitrogen content of the sewage. The nitrogen content also had a high correlation with the alkalinity, the content of orthophosphate and the total phosphorus content of the sewage.

A model for optimal coagulant dose

Above, the correlation between each separate sewage parameter and the optimal coagulant doses for ferric chloride and aluminium sulphate have been discussed. The control of the coagulant doses requires an equation for the prediction of the optimal amount of coagulant from the sewage parameters. This equation can be calculated from the measurements carried out earlier.

A multiple linear regression model was chosen. This linear regression model is given by:

$$\hat{y} = b_0 + b_1 x_1 + b_2 x_2 + \ldots b_k x_k,$$

in which

$\hat{y}$ = estimated value for the coagulant dose y;
x_i = sewage parameter i;
b_i = regression coefficient i.

The regression coefficients were selected by minimizing the sum of the squared residuals $\Sigma(y-\hat{y})^2$, the differences between each observed value y and its corresponding fitted value $\hat{y}$. A computer program written by Daniel & Wood (1971) was used. This computer program also selects which sewage parameter(s) is/are of importance for the equation. The most comprehensive approach for this selection of sewage parameters is to fit them into all possible equations and then to compare them. When a large number of alternative equations are being considered, it is imperative that some simple criterion of goodness or badness of fit be chosen to characterize each equation. In the above computer program this procedure is carried out by a so-called C_p-search. The C_p-value is a simple function of the residual sum-of-squares from each fitting equation. At a certain significance level (γ) the estimated coagulant dose is:

$$\hat{y} \pm t_f\left(\frac{\gamma}{2}\right)\cdot\hat{\sigma}\sqrt{\frac{1}{N}+\frac{(x_0-\bar{x})^2}{\Sigma(x_i-\bar{x})^2}},$$

in which:

t_f = Student's distribution with f residual degrees of freedom;
$\hat{\sigma}$ = residual root-mean-square;
N = number of experiments.

In practice the controlling sewage parameters have to fulfil the following requirements: the parameters have to be determined continuously, in short time and their determination must be reliable.

The determination of the total phosphorus content of a raw sewage is possible, but this determination costs about 20 min. The determination of orthophosphate in sewage takes about 6 min. The alkalinity, which shows third best correlation coefficient with the optimal coagulant doses, is easy to determine, but not continuously; however the sampling frequency can be very high (*ca.* 20 times h^{-1}). The Kjeldahl-nitrogen content is not easily determined continuously in wastewater, but the specific conductivity poses no problems.

The results of the computer calculations are given in Table 5 for ferric chloride as coagulant for the "inflexion point optimal coagulant dose" y_1 and for the "90% optimal dose" y_2. The results of the calculations for aluminium sulphate as coagulant are given in Table 6.

The regression coefficients (b) of the equation $\hat{y} = b_0 + b_1x + \ldots b_kx_k$ are presented in Tables 5 and 6. The multiple correlation coefficient (r) expresses the correlation between the sewage characteristics (x) and the optimal coagulant dose y_1 or y_2. To ensure that in 95% of all cases the optimal coagulant dose is reached or exceeded a confidence band has been calculated; this value is the amount of coagulant in mmol l^{-1} that has to be added on top of the optimal coagulant dose calculated from the equation on bases of the sewage parameters.

The computer calculations show that total phosphorus content of the sewage is the best characteristic for calculating the optimal coagulant dose. The addition of any other sewage parameter, besides the total phosphorus concentration, does not improve the calculation of y_1 or y_2 from a statistical point-of-view. The correlation coefficient between the "inflexion point optimal dose" y_1 and the total-P content was lower than the correlation coefficient between the "90% optimal dose" y_2 and the total phosphorus concentration of the sewage. As mentioned before the automatic total P-analysis of sewage is possible but takes about 20 min and requires a rather complicated apparatus.

Therefore it was calculated, which of the parameters ortho-P, pH, alkalinity, specific conductivity and transmission can be applied to determine the optimal coagulant dose. Tables 5 and 6 show the pH plus the alkalinity are of great importance for calculating the "inflexion point optimal dose". The pH plus the alkalinity showed a higher multiple correlation coefficient with the optimal coagulant dose y_1 than the total phosphorus concentration of the sewage did, but the confidence band with the pH and the alkalinity was wider than with the total phosphorus content. From a statistical point-of-view, the ortho-P concentration of the sewage is the second best parameter for calculating the "90% optimal coagulant dose" y_2. This applies for both coagulants.

Table 5. Computer results for ferric chloride as coagulant. Batch experiments

Average opt. dose* according to y_1 or y_2 (mmol Fe l^{-1})	Regression coefficients (b) in coagulant control with					Multiple correlation coefficient	Confidence band with 0.95 interval (mmol Fe l^{-1})
	b_0	Total-P	Ortho-P	Alkalinity	pH		
y_1 0.691 ± 0.400	0.153	0.024	—	—	—	0.560	±0.370
	0.226	—	0.029	—	—	0.384	±0.462
	0.091	—	—	0.086	—	0.449	±0.439
	−2.712	—	—	—	0.463	0.572	±0.389
	−2.500	—	—	0.053	0.389	0.628	±0.479
y_2 1.048 ± 0.374	0.223	0.037	—	—	—	0.919	±0.168
	0.167	—	0.056	—	—	0.780	±0.279
	0.165	—	—	0.127	—	0.701	±0.319
	0.326	—	—	—	0.100	0.130	±0.417
	0.864	—	—	0.136	−0.105	0.712	±0.399

* ± Standard deviation.

Table 6. Computer results for aluminium sulphate as coagulant. Batch experiments

Average opt. dose* according to y_1 or y_2 (mmol Al l^{-1})	Regression coefficients (b) in coagulant control with					Multiple correlation coefficient	Confidence band with 0.95 interval (mmol Al l^{-1})
	b_0	Total-P	Ortho-P	Alkalinity	pH		
	0.133	0.021	—	—		0.688	±0.228
	0.104	—	0.032		—	0.580	±0.283
y_1 0.606 ± 0.283	−0.044	—	—	0.094	—	0.673	±0.255
	−1.127	—	—	—	0.240	0.404	±0.304
	−0.791	—	—	0.085	0.112	0.696	±0.345
	0.192	0.028	—	—	—	0.815	±0.199
	0.062	—	0.047	—	—	0.783	±0.239
y_2 0.807 ± 0.307	0.061	—	—	0.107	—	0.704	±0.201
	0.926	—	—	—	−0.016	0.024	±0.358
	1.420	—	—	0.124	−0.204	0.764	±0.303

* ± Standard deviation.

The addition of iron to a concentration of about 0.4 mmol Fe l^{-1} or of 0.3 mmol Al l^{-1} on top of the calculated optimal coagulant dose, in order to assure that the real optimal coagulant dose was achieved, never showed any disadvantageous effect on the removal of TOC or phosphorus in the coagulation–flocculation process.

Verification

These computer calculations based on batch experiments were verified in two pilot plants, which had proved to give the same removal efficiency for TOC, DOC and phosphorus compounds with the same coagulant dose. In one pilot plant a constant dose of coagulant per m^3 influent was set, in the other pilot plant the coagulant dose was related to a sewage parameter. The two plants were operated identically with the same wastewater as used for the batch experiments and with a constant influent flow, under various weather conditions. Ferric chloride was used as coagulant and the flocculation pH was adjusted to 5.3. For practical reasons the orthophosphate concentration of the sewage was chosen as parameter with which the 90% optimal coagulant dose was calculated.

The orthophosphate was continuously measured with a Technicon autoanalyser. After dilution the sample was filtered through a 2 μm laboratory filter tube (Whatman size A1). The deflection of the recorder was transformed into a signal for a steerable pump, dosing ferric chloride. According to Table 5 the following equation applies with a confidence band having a 0.95 interval.

$y_2 = 0.167 + 0.056\{\text{ortho-P}\} \pm 0.279$, in which
y_2 = the 90% optimal dose for ferric chloride (mmol l^{-1} of Fe)
$\{\text{ortho-P}\}$ = the orthophosphate concentration in the sewage (mg P l^{-1}).

In order to achieve in 95% of all cases the calculated y_2, 0.279 mmol l^{-1} of iron has to be added extra. The equation therefore can be written as follows:

$y_2^* = 24.90 + 3.11\{\text{ortho-P}\}$, in which
y_2^* = the 90% optimal dose for ferric chloride (mg Fe l^{-1})
$\{\text{ortho-P}\}$ = the orthophosphate concentration of the sewage (mg P l^{-1}).

On average the orthophosphate content of the sewage, see Table 1, was 16.0 mg P l^{-1} so that on average 74.7 mg l^{-1} of iron was required. The maximal orthophosphate concentration of the sewage, also determined in the batch experiments, amounted to 28.0 mg P l^{-1}. This requires a 90% optimal coagulant dose of 112 mg Fe l^{-1}.

Previous experiments (Leentvaar *et al.*, 1978) have shown that in order to achieve the maximal TOC removal at least 125 mg Fe l^{-1} has to be added. This dose of 125 mg Fe l^{-1} was applied; the other pilot plant worked with a fixed dose of 24.90 mg Fe l^{-1} and with a variable dose of 3.11 times the orthophosphate concentration in the crude sewage. From Table 7 it can be concluded that the amount of ferric chloride related to the orthophosphate concentration of the wastewater results in the same removal efficiency with respect to TOC as in the second pilot plant to which a fixed amount of ferric chloride was added. This conclusion was checked with a *t*-test statistic. The standard deviation (±) was a little higher for the variable dose than for the fixed dose per litre wastewater. This result is an indication that the computer calculations of the 90% optimal coagulant dose plus the amount of coagulant needed for the 0.95 confidence band can achieve a considerable coagulant reduction of 35%.

CONCLUSION

In almost all experiments the optimal coagulant dose, measured in terms of mmol l^{-1} of Fe or Al for aluminium sulphate as coagulant is lower than for ferric chloride. The curve of transmission vs coagulant dose was steeper for aluminium sulphate than for ferric chloride. This shows that for the

Table 7. Verification of computer calculations in pilot plant experiments, with ferric chloride as coagulant. (Number of data = 40)

Coagulant dose (mg Fe l^{-1})	Average coagulant dose (mg Fe l^{-1})	Influent* TOC (mg C l^{-1})	%-Removal* (%)
125.0	125.0	168.3 ± 41.3	64.6 ± 9.7
24.90 + 3.11{ortho-P}	84.4	168.3 ± 41.3	64.3 ± 12.4

* ± Standard deviation.

domestic sewage of the village Bennekom, aluminium sulphate is more effective as coagulant than ferric chloride. This result applies for both removal of TOC and for removal of phosphorus but contradicts the findings of Hsu (1976), who found that in simple systems ferric chloride is more effective than aluminium sulphate in precipitating phosphate in a solution. There is not a good explanation for the high correlation between the total phosphorus content of the sewage and the optimal coagulant dose.

It is possible that the metal-phosphorus-complex forms the nucleus for the absorptive and sweep coagulation. The "90% optimal value" determined in terms of transmission showed a remarkable correlation in terms of TOC and phosphorus removal. The study showed that the "90% optimal value" (y_2) could be more accurately determined than the "inflexion point optimal value" (y_1).

It is possible to estimate the required coagulant dose from the parameters of the sewage. Especially the total phosphorus concentration showed a high correlation with the optimal coagulant dose. The disadvantage of the phosphorus determination is the rather expensive equipment and the long time needed for the analysis. On the other hand a combination of the alkalinity and the pH gives a reliable estimate of the optimal coagulant dose y_1 for both ferric chloride and aluminium sulphate as coagulant. For the estimation of the "90% optimal coagulant dose", the alkalinity of the sewage can be determined.

Experiments in two pilot plants showed that the computer calculations based on batch experiments can be used quite well in continuous flow coagulation-flocculation plants. A comparison between a constant coagulant feed of 125 mg Fe l^{-1} and a dose of 24.9 + 3.11 times the orthophosphate concentration of ferric chloride leads to the same removal with respect to TOC and gives a coagulant reduction of 35%. Especially for coagulation-flocculation plants, connected to a combined sewerage system this method of coagulant dose in relation to characteristical sewage parameters is of great economic importance.

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7. DESIGN CRITERIA FOR A COAGULATION-FLOCCULATION PLANT FOR SEWAGE

By Jan Leentvaar*, Robert E. Roersma and Theo S. J. Ywema****

This article describes experiments on batch and pilot plant scale aimed at determing some design criteria for a coagulation-flocculation plant, which operates with domestic wastewater. Particular attention was paid to detention time and mixing intensity in rapid mix unit and flocculator, number of flocculator compartments and to surface loading and detention time in the sedimentation tank.

The experiments showed that pilot plant experiments are necessary when a full-scale coagulation-flocculation plant has to be designed.

Konstruktionsmerkmale für Flockungsanlagen im Abwasserbereich. Im Becherglas- und halbtechnischem Maßstab wurden Flockungsexperimente durchgeführt. Damit sollten Bemessungsgrundlagen für den Bau einer Flockungsanlage für kommunales Abwasser erhalten werden. Im Mittelpunkt der Arbeiten standen die Verweilzeit und die Rührintensität in der Mischkammer und im Flocculator sowie die Anzahl der Flocculatoreinheiten und der Oberflächenbelastung und der Verweilzeit in den Absetzbecken.

Die Arbeit zeigt, daß Erfahrungen mit der Pilotanlage für den Entwurf einer großtechnischen Flockungsanlage notwendig sind.

Introduction

Impurities in wastewater vary in size and type. The removal of a large portion of these impurities in wastewater treatment is accomplished by sedimentation. As many particles are too small for gravitational settling alone to be effective, aggregation by coagulation-flocculation of these particles into large, more readily settable aggregates can increase the portion of sedimentation in the total purification process. Coagulation-flocculation for the removal of turbidity and colour is commonplace in purification of surface water and research on this process has been considerable.

Earlier experiments with domestic sewage (*Leentvaar* et al. [1]) obtained on batch scale and in a small scale pilot plant with a flow of 0.06 $m^3\ h^{-1}$ indicated a need to check these results in a larger pilot plant.

The aim of this study is to obtain some design criteria for a coagulation-flocculation plant that operates with domestic sewage. Parallel to these pilot plant experiments jar-tests were carried out to determine the optimal detention time in the different units and the optimal mixing intensity.

Experimental Setup

The experiments were carried out with raw unsettled sewage of the village Bennekom, which is mainly of domestic origin. This wastewater is of medium strength. See Table 1.

Table 1. Average composition of the raw sewage of the village Bennekom

pH	7.25
Alkalinity (meq $HCO_3^-\ l^{-1}$)	7.02
Spec. conductivity ($\mu S\ cm^{-1}$)	980
Transmission (%)	30
Suspended solids ($mg\ l^{-1}$)	370
TOC ($mg\ C\ l^{-1}$)	170
DOC ($mg\ C\ l^{-1}$)	77
COD ($mg\ O_2\ l^{-1}$)	420
BOD_5 ($mg\ O_2\ l^{-1}$)	190
Ortho-P ($mg\ P\ l^{-1}$)	15
Total-P ($mg\ P\ l^{-1}$)	22
Kjeldahl-N ($mg\ N\ l^{-1}$)	85

Batch coagulation-flocculation experiments were carried out in square 2 l Plexiglass vessels with a cross-sectional area of $10 \times 10\ cm^2$.

The standard test procedure was as follows:

1. Mixing with a turbine type stirrer at 660 rev min^{-1}, which gave a G value of 680 s^{-1}.
2. Addition of coagulant (40% w/w ferric chloride solution) and adjustment of pH over a 60 s period at 660 rev min^{-1} (rapid mix).
3. Flocculation for 30 min with a propeller type stirrer at 67 rev min^{-1} ($G = 28\ s^{-1}$).
4. Sedimentation for 30 min.

The G value was measured with a pilot scale dynamometer as described by *Leentvaar & Ywema* [2]. After sedimentation, a sample of about 100 ml was taken at half height of the tank, of which the optical transmission was determined at 620 nm wavelength with a cuvette diameter of 2 cm. In addition sometimes the TOC was determined. According to previous work (*Leentvaar* et al. [3]), a high correlation exists between optical transmission and TOC of the sample after coagulation-flocculation.

Pilot plant experiments were carried out in two identical plants; see Fig. 1. The flow of the sewage was adjustable from 0.8 to 3.0 $m^3\ h^{-1}$.

The pilot plant consists of a rapid mix unit in which the wastewater enters tangentially and is mixed with the coagulant solution which drops into the vortex of water. See Fig. 2.

In this unit sodium hydroxide solution is added too, if the pH reaches values below 5.3.

After this initial vigorous mixing of coagulant and sewage the liquid enters a plug flow flocculator with 6 reactors.

The flocculator can be modified to reduce the number of reactors. A pH-electrode is placed in the first flocculation compartment. Each reactor has a volume of 100 l and is stirred with a gate type stirrer.

The liquid is stirred with 26, 17, 13, 11, 8 and 5 rev min^{-1}, which equals a G value of 97, 55, 39, 30, 21 and 12 s^{-1}

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*Min. of Transport and Public Works, Delta Dept., Erw. Res. Sec., P.O.B. 439, Middelburg, the Netherlands.

**Department of Water Pollution Control, Agricultural University, Wageningen, the Netherlands.

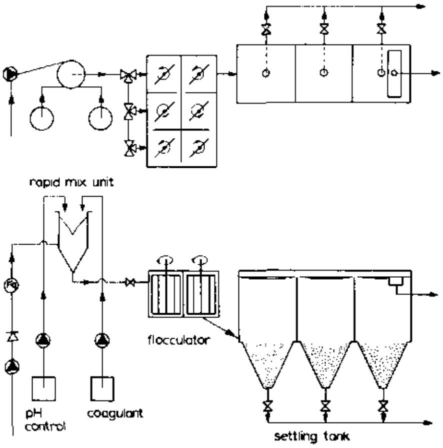

Fig. 1. Pilot plants used in this study

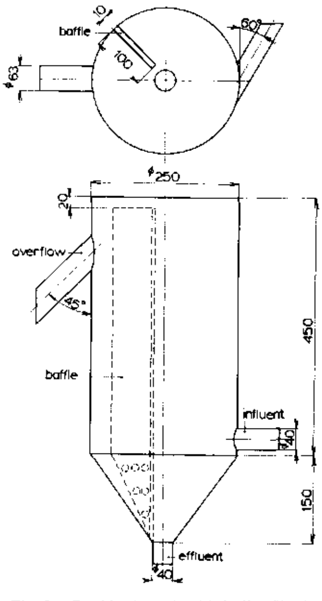

Fig. 2. Rapid mix tank with baffle. Size in mm

respectively. The G values in the reactors of the pilot plant were determined with a torquemeter (HBM T2/20).

After the flocculation stage the water flows into a sedimentation tank with a volume of 2.175 m^3 and a surface of 1.841 m^2. The sedimentation tank can be modified into a tank with volume and surface of 1.450 m^3 and 1.227 m^2 or with volume and surface of 0.725 m^3 and 0.614 m^2. The settled sludge is drawn off continuously.

From influent and effluent of the pilot plants composite samples were taken, twice daily, which were analysed on the TOC and the optical transmission.

In the pilot plant experiments ferric chloride (40% w/w soln.) was used as coagulant too.

The residence time destribution in the rapid mix unit and in the flocculator was determined by adding a constant flow of a sodium fluorescein solution to the water entering the apparatus at a given water flow at t_0 and measuring the absorbance of the outcoming water at 454 nm with the time. In this way a cumulative distribution curve (F-curve) is obtained which was analysed according to the method of *van der Laan* [4].

Results and Discussion

Batch experiments

The design of rapid mix unit is determined by reactions occurring in the destabilization of the colloidal particles to be aggregated.

With an inorganic salt as coagulant, polymers are formed in the water being treated, after which they can adsorb on the surface of the colloidal particles.

Virtually instantaneous mixing of coagulant and water is desirable when Fe-III or Al-III salts are used as coagulants because (1) rate of formation of polymers is very fast, (2) the production of uniform coagulant pieces requires a uniform pH and coagulant dosage in the system, and (3) rates of adsorption of these small polymers are also fast.

Detention times of 1 second or more are unnecessary, since these reactions are complete in a second or less (*Weber* [5]).

Previous experiments (*Leentvaar* et al. [1, 2]) have shown that to achieve the maximal TOC removal under all wastewater conditions at least 125 mg Fe l^{-1} has to be added, while on average 75 mg Fel^{-1} is required in order to obtain about 90% removal of removable TOC. Batch experiments showed that the differences in removal due to flocculation were better perceptible when the coagulant dose was not too large. Therefore in the batch experiments only 10 mg Fe l^{-1} was used to gain the greatest differences in turbidity and TOC removal under various treatment procedures. In several jar tests the optimal rapid mix period and intensity were determined. The tests were carried out with fresh sewage according to the standard procedure, only the rapid mix period and intensity being varied.

Fig. 3 shows, that a short mixing period of about 7 s was the most favourable rapid mix period at a G value of 680 s^{-1}. At lower G values during the rapid mixing a very short period was also favourable. Only at very low G values of about 50 s^{-1} during the mixing of coagulant and water was no optimal mixing time perceptible.

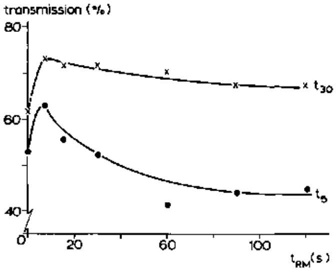

Fig. 3. Influence of rapid mix period on coagulation-flocculation performance. The transmission of the supernatant was measured after 5 (t5) and after 30 minutes (t30) of sedimentation.
G value during rapid mix: 680 s^{-1}. Batch experiments

Studies on the time needed for complete mixing of the liquid in the square vessel showed that with a G value of 680 s^{-1}, 2 s were needed. Therefore a rapid mixing period less than 2 s is unfavourable.

Fig. 4 shows that an intensive mixing gives a higher turbidity removal. However above a G value of about 700 s^{-1} air bubbles appeared in the system, which reduced coagulation-flocculation.

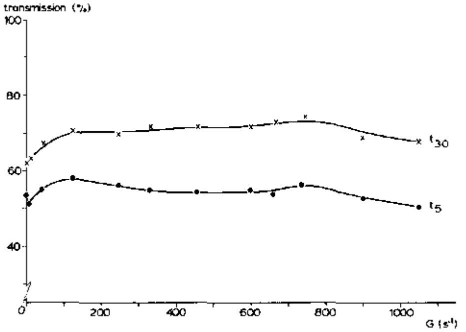

Fig. 4. Influence of rapid mixing intensity on coagulation-flocculation performance during a rapid mixing period of 7 s.
The transmission of the supernatant was measured after 5 (t5) and after 30 minutes (t30) of sedimentation. Batch experiments

A combination of period and intensity of the rapid mix phase is presented in Fig. 5, which shows that a short period, e. g. 7 s compared with a period of 60 s, in combination with a relative high G value of about 700 s^{-1} is favourable for the batch experiments.

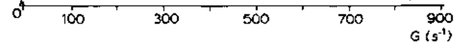

Fig. 5. Influence of mixing intensity and period [7 (RM7) and 60 s (RM60)] on coagulation-flocculation performance. The transmission of the supernatant was determined after 5 (t5) and after 30 minutes (t30) of sedimentation. Batch experiments

Agitation often accelerates aggregation of destabilized particles. Flocculation tanks are designed to provide interparticle contacts. Generally these contacts are brought about by velocity gradients that are produced within the fluid by hydraulic or mechanical means, which can be expressed in terms of G values. The design of the flocculators involves the selection of velocity gradients, reactor configuration and detention time in order to produce aggregates of a size suitable for removal from suspension e. g. in a settling tank. In series of batch experiments the optimal flocculation period and mixing intensity were determined. Fig. 6 shows that the minimum flocculation period in jar tests was about 6 minutes.

The influence of the G value during flocculation is illustrated in Fig. 7. The optimal G value in coagulation-flocculation for 30 min and afterwards sedimentation for 30 min was

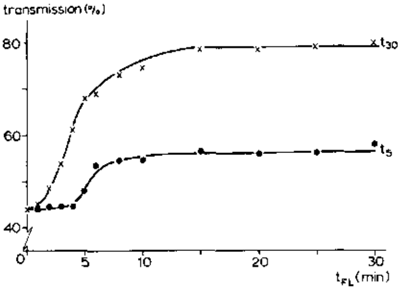

Fig. 6. Influence of flocculation period (t_{FL}) on coagulation-flocculation performance. Batch experiments

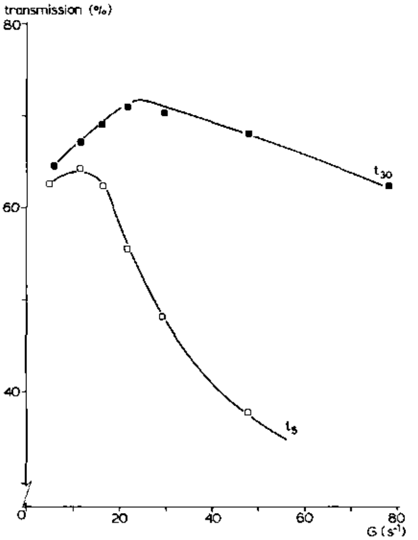

Fig. 7. Influence of G value during flocculation on coagulation-flocculation performance. Rapid mix period 7 s at 680 s^{-1}. Batch experiments

Table 2. Coagulation-flocculation of raw sewage with ferric chloride. Batch experiments at pH = 5.3. Number of experiments 22

Coagulant dose ($mg Fe l^{-1}$)	Influent TOC ($mg C l^{-1}$)	Effluent TOC ($mg C l^{-1}$)	TOC removal (%)
1.9	163 ± 63	141 ± 61	15 ± 13
3.9	163 ± 63	138 ± 55	16 ± 12
7.8	163 ± 63	123 ± 46	24 ± 14
15.5	163 ± 63	102 ± 35	36 ± 15
31.0	163 ± 63	88 ± 28	44 ± 12
62.0	163 ± 63	70 ± 20	55 ± 11
93.0	163 ± 63	67 ± 24	58 ± 9
125.0	163 ± 63	67 ± 23	57 ± 11
155.0	163 ± 63	63 ± 22	60 ± 8
186.0	163 ± 63	61 ± 24	62 ± 9

± Standard deviation

about 25 s^{-1}. A higher G value during flocculation caused a smaller turbidity removal. The influence of G value on flocculation is higher with a rapid mix period of 7 s than with a period of 60 s at 680 s^{-1}. A downward tapered velocity gradient, as suggested by *TeKippe* and *Ham* [6] had no advantageous effect on turbidity or TOC removal.

For the comparison of batch experiments with pilot plant experiments also TOC of sewage and supernatant after sedimentation was measured. See Table 2.

Pilot plant experiments

Pilot plant studies were carried out in order to evaluate data found in batch experiments and to acquire data for design of the different units.

In wastewater treatment the colloidal particles are generally fragile and easily ruptured. Vigorous agitation, while providing for uniform production and adsorption of metal coagulant species, may also generate a considerable amount of additional surface area, which will in turn require additional coagulant or breakdown the already formed flocs. Here less vigorous or shorter agitation could be preferable. In order to achieve the maximal TOC removal under all circumstances at least 125 mg Fe l^{-1} has to be added to the sewage. This dose of 125 mg Fe l^{-1} was applied in both pilot plants (*Leentvaar* et al. [1]). The performance of the two pilot plants was identical over a 2-month period with respect to TOC, DOC, ortho-P and total-P removal under different weather conditions. See Table 7, first line. From each pilot plant experiment the corresponding series of removal percentages in both pilot plants were analysed by a t-test statistic in order to calculate whether there was a signifcant difference between both series of data at a two-sided significance level of 0.05.

Rapid mix unit

The influence of rapid mixing on coagulation-flocculation of sewage on pilot plant scale was examined in two series of experiments: **1** with and without a rapid mix unit and **2** with and without baffle in the rapid mix unit. During these experiments both pilot plants, except for the rapid mix unit, were identical. The wastewater flow was 2.8 $m^3 h^{-1}$, the flocculator consisted of 6 reactors and the surface loading of the sedimentation tank amounted to 1.5 m h^{-1}. With the pilot plant without rapid mix unit the coagulant was dosed in the first flocculator reactor. The mixing intensity in both pilot plants was equal in the corresponding flocculator reactors. Table 3 illustrates the results of the experiments on residence time distribution in the rapid mix unit with/without baffle with a sodium fluorescein solution as tracer.

Table 3. Average detention time (τ) in the rapid mix unit, at a wastewater flow of 2.8 $m^3 h^{-1}$; with/without baffle

Baffled	τ (s)	with variance σ^2 (s^2)
–	4.81	16.23
+	3.03	1.80

The presence of the baffle has two influences: 1) more vigorous mixing of wastewater and coagulant and 2) shorter detention time with less variation.

Table 4 shows that there was an important decrease in TOC removal when a rapid mix unit was not applied. There also was an increase in TOC removal when the rapid mix tank was baffled. These differences in TOC removal were significant from a statistical point-of-view.

Table 4. Pilot plant experiments on the influence of rapid mixing on coagulation-flocculation performance (N = 12)

Plant No.	Influent TOC ($mg C l^{-1}$)	Rapid mix unit	Baffled	TOC removal (%)	Difference significant
1	138 ± 40	+	–	44 ± 13	+
2	138 ± 40	–	–	34 ± 16	
1	178 ± 36	+	–	54 ± 9	+
2	178 ± 36	+	+	58 ± 6	

± Standard deviation

Additional experiments however showed that this change in residence time in the rapid mix vessel was of minor importance when compared with the effect of mixing intensity of wastewater and coagulant. Batch experiments confirmed these findings as illustrated in Fig. 5.

Flocculator

The pilot plant experiments in which the flocculator was studied in more detail were foccused on the effect of the number of reactors of the flocculator and perforce on the effect of the average detention time of the sewage in this unit; as in all experiments the surface loading of the sedimentation tank was kept at 1.5 m h^{-1}. In this particular series of experiments both plants worked with a rapid mix unit without baffle. One plant always worked with a rapid mix unit without baffle and always worked with six flocculator compartments, individually stirred with tapered decreasing mixing intensity.

In the other plant the number of flocculator reactors and therefore the detention time was modified between six and one. For technical reasons it was not possible to work with one flocculator reactor. Here the first compartment was stirred while the second was not agitated.

For each situation the average detention time and the theoretical number of completely mixed flow reactors (CMF) were calculated from the distribution function of the fluid according to the method of *van der Laan* [4].

See table 5.

Table 5. Average detention time (τ) and number of completely mixed flow reactors (CMF) in the flocculators as calculated from the distribution function of the sewage

Sewage flow ($m^3 h^{-1}$)	Nr. of flocculator compartments	G value (s^{-1})	τ (min)	Nr. of CMF
2.65	6	97/55/39/30/21/12	10.7	4.0
1.85	4	97/55/21/12	9.4	2.5
2.78	4	97/55/21/12	6.4	2.5
1.85	3	55/21/12	7.7	2.4
1.85	2	97/12	4.9	1.4
1.85	1 1)	97/0	5.0	1.5

1) Two compartments: one stirred and one at rest

O'Melia [7] described the rate of orthokinetic flocculation as:

$$\frac{dN}{dt} = -\frac{4}{\Pi}\alpha G N \Omega$$

in which

N : total concentration of particles in suspension at time t.

α : collision efficiency factor, representing the fraction of the total number of collisions which are successful in producing aggregates.

$\bar{G}$: mean velocity gradient as provided by hydraulic or mechanical means.

Ω : the floc volume fraction.

According to this formula the reaction is of first-order. The total detention time (t_x), required to achieve a desired level of performance for x well-mixed tanks in series may be determined according to

$$\bar{t}_x = \frac{\Pi x}{4\alpha\bar{G}\Omega}\left[\left(\frac{N_0}{N_x}\right)^{1/x} - 1\right] \qquad \text{in which}$$

N_0 : the concentration of (colloidal) particles in the influent to the first tank or compartment

N_x : the concentration of particles in the effluent from the last tank.

According to this formula a single, large well-mixed tank cannot perform as well as a number of smaller flocculators of equal total volume placed in series.

In order to determine the minimum number of flocculators this number was gradually decreased.

Table 6 illustrates that in coagulation-flocculation of Bennekom sewage there is no need for more than two flocculator reactors as the TOC removal does not differ significantly.

Table 6. Pilot plant experiments on the influence of number of flocculator reactors on coagulation-flocculation performance. Surface loading of the sedimentation tank 1.5 m h^{-1}. Other parameters as in Table 5

Plant No.	Nr. of flocc. reactors	τ (min)	Influent TOC (mg C l^{-1})	TOC removal (%)	Difference significant
1	4	9.4	184 ± 56	67 ± 11	–
2	6	10.7	184 ± 56	65 ± 13	
1	4	6.4	190 ± 20	51 ± 5	–
2	6	10.7	190 ± 20	55 ± 4	
1	3	7.7	199 ± 35	60 ± 7	–
2	6	10.4	199 ± 35	60 ± 7	
1	2	4.9	223 ± 58	54 ± 10	–
2	6	10.7	223 ± 58	56 ± 11	
1	1[1)]	5.0	133 ± 61	56 ± 13	+
2	6	10.7	133 ± 61	60 ± 13	

1) Two compartments: one stirred and one at rest

± Standard deviation

The minimal average flocculation time applied in the pilot plant experiments amounted to 4.9 minutes which gave a good TOC removal and is in accordance with the batch experiments.

Sedimentation tank

As the cost for the sedimentation tank is the most important part of the investment cost, this tank should be designed very carefully.

Pilot plant experiments were carried out in order to determine the maximum surface loading of the sedimentation tank. Sedimentation characteristics were evaluated in batch by placing 200 l coagulated wastewater in a settling cylinder with sampling points at different heights of the cylinder. The suspension was allowed to settle under quiescent conditions. The optical transmission was determined on samples withdrawn from several depths at different time intervals.

From these data the settling velocity at a known depth can be determined at a fixed degree of purification. For sedimentation tanks of the pilot plants with a depth of 1.8 m and a removal ratio of 95% the settling velocity was about 6 m h^{-1}. This value cannot be used in a horizontal flow sedimentation tank. A rule of thumb is to take a conversion factor of 1.7 to 2.0. In order to check this assumption experiments were carried out with various surface loadings in the settling tank of one plant, while the surface loading in the other plant was kept constant at 0.81 m h^{-1}. Table 7 gives a survey of the results of these experiments.

Table 7. Pilot plant experiments on the influence of surface loading (S) and average detention time (τ) in the sedimentation tank on coagulation-flocculation performance. Number of flocculator compartments: 6

Plant No.	Sewage flow (m^3 h^{-1})	S (m h^{-1})	τ (h)	Influent TOC (mg C l^{-1})	TOC removal (%)	Difference significant
1	1.50	0.81	1.45	182 ± 12	60 ± 8	–
2	1.50	0.81	1.45	182 ± 12	61 ± 9	
1	2.00	1.09	1.09	223 ± 46	62 ± 13	–
2	1.50	0.81	1.45	223 ± 46	60 ± 12	
1	1.33	1.08	1.09	128 ± 64	60 ± 9	–
2	1.50	0.81	1.45	128 ± 64	58 ± 13	
1	1.77	1.44	0.82	202 ± 30	55 ± 9	–
2	1.50	0.81	1.45	202 ± 30	58 ± 9	
1	2.48	2.02	0.58	134 ± 61	56 ± 9	+
2	1.50	0.81	1.45	134 ± 61	58 ± 7	

± Standard deviation

Table 7 shows that a surface loading of the sedimentation tank of 2 m h^{-1} in combination with a detention time of about 35 minutes is too high for a sufficient clarification. Although the TOC removal percentages at the surface loading of 2 m h^{-1} do not differ much, the difference is obvious from a statistical point of view.

Weber [5] reported that a frequently used value for the surface loading of iron floc was about 3 m h^{-1} with a detention period in a 3 m tank of 10 h.

For the Bennekom sewage coagulated-flocculated with ferric chloride a surface loading of 1.50 m h^{-1} was required for optimal clarification and so results a conversionfactor of about 4.

Floc blanket clarifier

A special case of flocculation is provided by the floc blanket clarifier. This aspect of flocculation was simulated by operating one conventional pilot plant with a floc blanket to half height of the sedimentation tank. Both pilot plants were operated with a sewage flow of 2.65 m^3 h^{-1}, a rapid mix unit without baffle and six flocculator reactors. The surface loading of both sedimention tanks was 1.50 m h^{-1}. In these particular experiments the coagulant dose amounted to 100 mg Fe l^{-1}. Table 8 summarizes the results with and without sludge blanket in the sedimentation tank. The difference between the TOC removal of both plants is very large.

Table 8. Pilot plant experiments on the influence of a floc blanket in the sedimentation tank. Number of data: 13

Floc blanket	Coagulant dose (mg Fe l^{-1})	Influent TOC (mg C l^{-1})	TOC removal (%)	Difference significant
–	100	166 ± 56	66 ± 9	+
+	100	166 ± 56	57 ± 8	

± Standard deviation

Sludge

The sludge properties did not differ with the number of flocculator reactors or the surface loading of the sedimentation tank applied.

At a coagulant dose of 125 mg Fe l^{-1} 0.100 l sludge per l wastewater was formed with a dry solids content of 6000 mg l^{-1} at a settling period of about 90 minutes. The suspended solid concentration in the sewage, however, was on average 370 mg l^{-1} and ranged from 2 to 3390 mg l^{-1}.

Conclusion

In the design of a coagulation-flocculation plant for domestic wastewater of the village Bennekom batch and continuous flow experiments turned out to be supplementary. The influence of the detention time of sewage and coagulant in the rapid mix unit on coagulation-flocculation was determined mainly in batch experiments. These experiments showed that a short and intensive mixing period of sewage and coagulant was favourable, although air burst within the fluid was disadvantageous. It is evident that the rapid mix period in the reactor should be equal or longer than the mixing time required for complete mixing of the liquid in the tank. In batch experiments a G value of about 700 s^{-1} for 7 s gave the best results. In pilot plant studies it was nearly impossible to measure exactly the G value of the rapid mix unit. Also in the pilot plants a higher G value (e.g. tank with baffle) was advantageous together with a plug flow system.

The design of the flocculator involves selection of reactor configuration, velocity-gradients and detention time. Previous experiments and general design foundations indicated that square tanks would be favourable. At the start of the pilot plant experiments a downward tapered velocity-gradient in 6 flocculator reactors was chosen. However it was not disadvantageous to use only two flocculator compartments with G values of 97 and 12 s^{-1}. In batch experiments no improvement could be obtained with a downward tapered veloticy-gradient instead of one constant G value of 28 s^{-1}. Batch experiments and quiescent column settling tests did not give a good value for the surface loading of the horizontal flow sedimentation tank. The design of this unit could be obtained in pilot plant experiments. The maximum surface loading in the pilot plant was 1.5 m h^{-1}, with an average detention time of about 50 minutes in a sedimentation tank with a depth of 1.8 m.

The pilot plant experiments indicated that the TOC removal increased strongly using a floc blanket in the sedimentation tank. With respect to TOC removal the batch experiments and the pilot plant studies without floc blanket and with identical coagulant dose showed good agreement, as illustrated in Table 9.

Table 9. Comparison between batch coagulation-flocculation experiments and pilot plant studies at a coagulant dose of 125 mg Fe l^{-1}. The pilot plant was operated with 2.65 m^3 sewage h^{-1}, 6 flocculator reactors and a surface loading of the sedimentation tank of 1.50 m h^{-1}

	Number of data	Influent TOC (mg C l^{-1})	Effluent TOC (mg C l^{-1})	TOC removal (%)
Batch	22	163 ± 63	67 ± 23	57 ± 11
Pilot plant	64	179 ± 55	78 ± 25	57 ± 11

± Standard deviation.

The sludge properties were not influenced strongly by the design variations of flocculator or sedimentation tank.

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8. PHYSICO-CHEMICAL TREATMENT OF MUNICIPAL WASTEWATER. COAGULATION-FLOCCULATION

J. Leentvaar, W. G. Werumeus Buning and H. M. M. Koppers
Department of Waterpurification, Agricultural University, Wageningen, The Netherlands

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Abstract—This article traces the possibilities of physico-chemical treatment of domestic sewage with particular attention to coagulation–flocculation processes. As coagulants the following have been used: ferric chloride, hydrated lime and alum. Different types of coagulant aids have been used too. Besides pilot-plant experiments, a large number of batch experiments has been carried out in order to determine the range of optimal doses of coagulants/coagulant aids/pH and so on. The fate of specific organic and inorganic components (proteins, detergents, low organic acids, phosphorus, nitrogen) as well as TOC, BOD and COD in this chemical treatment have been studied. The suspended and most of the colloidal fractions have efficiently been removed. A considerable fraction, which is defined as soluble, has been removed too. The significance of the findings for wastewater treatment processes have been discussed.

INTRODUCTION

It is well known that a well operated mechanical–biological wastewater treatment plant eliminates about 90% of the organic material based on COD. This is partially due to the fact that a small part of the compounds in the sewage is not biologically degradable and the growth of bacteria also creates a small amount of biologically inert matter. These compounds are called refractory (half-life time greater than two days) (Wuhrmann, 1972). Besides a diminution of the amount of total wastes discharged, physico-chemical treatment may offer a possibility to decrease the amount of "residual organic carbon" in the effluent (Roberts & Stumm, 1974). For the drinking water production from polluted riverwater and for the elimination of phosphorus from wastewater physico and/or chemical treatment methods are of great importance. Direct physico-chemical treatment of raw sewage without a biological step has been studied e.g. by Weber (1970); Zuckerman & Molof (1970); Cooper & Thomas (1974); Rebhun (1974). The first two studies have been carried out on low strength wastewater and the latter two reported about relatively strong municipal wastewater. This article refers to experiments carried out during more than two and a half years on physical–chemical treatment of medium strength domestic sewage.

Average influent—	COD and	$-BOD_5$ (mg O_2/l)
Weber (1970)	—	about 50
Zuckerman & Molof (1970)	195–568	105–164
Rebhun (1974)	1300	450
Cooper & Thomas (1974)	1065	450
Present study	460	171

The advantages of direct physico-chemical treatment compared with biological treatment of wastewaters are (Kossen, 1974):

extending phosphorus removal; better meeting of peak loadings; immediate start-up and shut-down; taking up less space; insensitive to toxic compounds in the wastewater.

The disadvantages are:

the use of chemicals; more complicated processing; more checking apparatus; possibility of H_2S-development in carbon columns, when using fixed beds in downflow; higher energy consumption.

For this reason Haskoning (consulting engineers), the Department of Water Purification of the Agricultural University and Norit N.V. (manufacturer of activated carbon) started a project in 1973 in order to develop a physico-chemical treatment plant for European municipal and industrial wastewaters.

Anticipating the construction of a pilot-plant with a flow of 2 m^3 h^{-1}, which was completed in October 1975, preliminary experiments have been started on batch scale and in a small pilot-plant. All experiments have been carried out with sewage of the village Bennekom, which is of domestic origin.

ANALYTICAL PROCEDURES

BOD, COD, total and ammonia nitrogen, phosphates and detergents have been determined according to Standard Methods (1965). Proteins have been determined using a modified Folin method with albumine as a standard. Volatile low organic acids have been determined on a gas-liquid chromatograph. The soluble fraction of the sewage and the effluent has been defined as the filtrate after membrane filtration with a 0.45 μm filter.

Thus the experimentally defined soluble fraction contains colloidal as well as soluble organic material. As polymers have been used: Superfloc A100, C100 and N100.

EXPERIMENTS

In the phase of the research reported here, chemical-flocculation–clarification has been studied as well in batch

Table 3. Chemical treatment of raw sewage with different alum dose. Batch experiments

pH	Coagulant dose (g Al/m³)	Coagulant-cost (f/m³)	Before treatment TOC	Before treatment DOC	After treatment TOC	After treatment DOC	% removal Total	% removal Soluble
5.5	4.1	0.01	165 ± 63	73 ± 28	132 ± 51	72 ± 28	19 ± 14	—
5.5	8.1	0.03	165 ± 63	73 ± 28	110 ± 46	72 ± 20	33 ± 16	1 ± 0
5.5	16.2	0.06	165 ± 63	73 ± 28	82 ± 28	70 ± 20	48 ± 12	5 ± 3
5.5	32.4	0.12	165 ± 63	73 ± 28	67 ± 25	57 ± 6	59 ± 10	22 ± 8
5.5	47.4	0.17	165 ± 63	73 ± 28	67 ± 23	55 ± 2	59 ± 9	24 ± 5
5.5	64.9	0.24	165 ± 63	73 ± 28	64 ± 22	59 ± 5	60 ± 8	19 ± 7
5.5	81.1	0.30	165 ± 63	73 ± 28	66 ± 22	55 ± 2	60 ± 10	24 ± 5

of 0.06 $m^3 h^{-1}$ and consists of a coagulation–flocculation tank, a Dortmund sedimentation tank, a multi-media sandfilter and an activated carbon column. See Fig. 6. After a few months an equipment for powdered activated carbon processes has been added. The average detention time of the wastewater in the coagulation–flocculation tank is 23 min and in the sedimentation tank about 1.5 h.

The rapid mixing of flocculants is obtained by injecting the chemicals into the sewage feed pipe. In the first flocculation-chamber the sewage stays on average 3 min and is submitted to a G-value of about 64 s^{-1} (92 rpm) by stirring with a propeller. In this flocculation-chamber is also placed the pH-electrode. In the second flocculation-chamber the sewage has an average detention time of 20 min and is submitted to a G-value of circa 19 s^{-1} (13 rpm).

Composite samples of the influent (raw wastewater) and of the sedimentation tank effluent have been collected. These samples have been taken daily three times per hour. This procedure has been executed for five days a week. In the continuous flow experiments three flocculants have been used: ferric chloride, hydrated lime and alum.

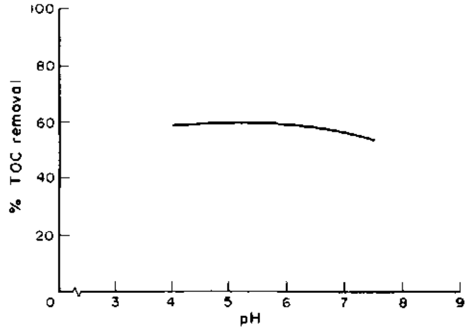

Fig. 5. Coagulation–flocculation with alum in batch experiments. The pH versus the percentage TOC removal at an alum dose of 47 mg Al/l.

The pilot-plant experiments on ferric chloride as coagulant have been carried out for 9 months. The ferric chloride used is a 41% w/w $FeCl_3$ solution. The pilot-plant studies have been started by adding a constant amount of ferric chloride to a constant flow influent. Soon it has turned out that the changes in the composition of the influent are so high that the flocculation often did not succeed, because of the low pH in the coagulation–flocculation tank when the sewage had been diluted with rainwater. This procedure has been left and has been changed over to a feed of ferric chloride related with the pH in the flocculation tank. That amount of flocculant has been dosed in the tank to reach a fixed pH-value. A presupposition of this way of adding ferric chloride is that the required feed of ferric chloride is proportional to the alkalinity of the sewage and that this magnitude is related to the concentration of pollution. Dependent on the pH and the alkalinity of the influent the dose of $FeCl_3$ ranges from 40 to 160 mg Fe/l sewage at a fixed pH-value in the flocculation tank of about 5.3. This way of coagulation–floccula-

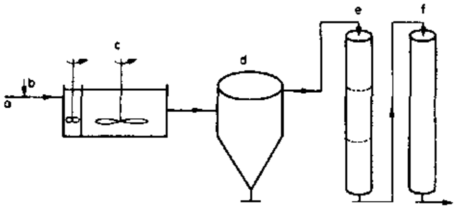

Fig. 6. Flow-scheme of the pilot-plant. a. influent; b. dosage of coagulant; c. coagulation-flocculation-tank; d. Dortmund sedimentation tank; e. sandfilter; f. activated carbon column.

Table 4. Removal of specific compounds with chemical treatment of sewage. Batch experiments

Component	Unit	Raw wastewater (total)	Percentage removal with Ferric chloride 75 mg Fe/l	Percentage removal with Hydrated lime at pH 11.0	Percentage removal with Alum 47 mg Al/l
BOD_5	mg O_2/l	248	63	59	59
COD	mg O_2/l	723	72	69	72
Proteins	mg/l as albumine	58	63	62	59
Ammonia	mg N/l	28	16	18	14
Organic N	mg N/l	54	6	10	7
Detergents	mg/l (anion-active)	15	56	47	74
Ortho-phosphate	mg P/l	10	99	99	99
Total-phosphate	mg P/l	31	96	94	97
Acetic acid	mg/l	44.5	0	12	4
Propionic acid	mg/l	8.5	−10	0	−19

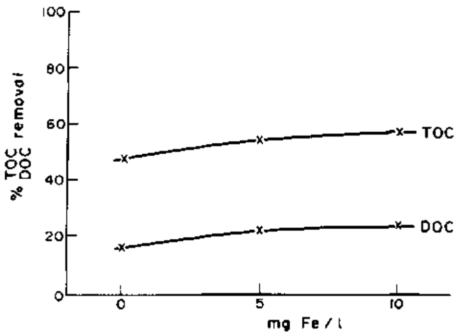

Fig. 7. Pilot-plant experiment with hydrated lime as coagulant at pH 11.0. The effect of ferric chloride as coagulant aid on the elimination of TOC and DOC.

tion is a rather expensive one. In the following experiments a constant amount of ferric chloride is dosed, in which the pH by means of $NaHCO_3$ and/or H_2SO_4 has been fixed at a pH of 5.3 or 7.7 in order to study the two parameters (pH and flocculant dose) independently.

The efficiency of the coagulation–flocculation of sewage with iron-III-chloride is higher at pH 5.3 (iron dosage on average 61 mg Fe/l) and the variation in percentage reduction is less than at pH 7.7.

These values are:

	Percentage removal of		
pH	Total organic carbon	Soluble organic carbon	Suspended solids (mg C/l)
5.3	54% ± 14	27% ± 12	93% ± 4
7.7	50% ± 24	19% ± 10	77% ± 11

The reduction of total phosphorus amounts in all cases to about 80%.

When coagulating with lime the process is determined by the pH. These experiments have been executed for 9 months. In the continuous flow experiments the influent shows also a wide variation in organic carbon content too. The experiments have shown that the eliminated amount of organic carbon increases accordingly as the influent TOC rises. The addition of small quantities of iron-III-chloride to the wastewater beside lime leads to some improvement of the effluent quality. See Fig. 7.

In order to improve the coagulation–flocculation process also recirculation of sludge from the sedimentation tank to the flocculation basin has been practised. The theories about orthokinetic flocculation indicate that by increasing the volume fraction of the particles the formation of bigger flocs is stimulated. In view of the wide variation in reduction with and without sludge recirculation in the flocculation process with lime a conclusion cannot be drawn whether sludge recirculation is positive or not. The total reduction of organic carbon from the influent by coagulation–flocculation with lime at pH 11.0 is 44% ± 15; with lime at pH 11.0 and 5 mg Fe/l as coagulant aid this percentage is 51% ± 13. The elimination of suspended solids is about 90%.

Table 5. Amount and dry solid content of the chemical–organic sludges produced at flocculation of domestic sewage with ferric chloride, lime and alum

Coagulation–flocculation with:	Volume sludge (in l) per liter sewage	Dry solids content g per liter sludge
Ferric chloride (75 mg Fe/l)	0.069	5.0
Hydrated lime (at pH 11.0)	0.025	25.0
Alum (47 mg Al/l)	0.065	4.5

For five months continuous flow experiments with alum as coagulant have been carried out. According to the results obtained from the batch experiments, the optimum dosage of alum in the pilot-plant is about 47 mg Al/l sewage.

It is known that the alum-floc is very fragile. Therefore during two months 1.2 ppm of a cationic polymer has been added as a coagulant aid. No significant effect on the TOC-removal has been found however. With alum as coagulant it has also been studied whether recirculating chemical–organic sludge has a positive effect on the reduction of organic carbon. This has not been proved to be a significant success. The total reduction of TOC at a dosage of 47 mg Al/l at pH 5.9 is on average 58% ± 10. The reduction of dissolved organic carbon is 24% ± 13. The removal of suspended solids is in all cases greater than 85% and on average 94%.

The three coagulants (ferric chloride, hydrated lime and alum) produce different amounts and types of chemical–organic sludge. The quantity and the solid content of the sludge (without any treatment) that flows out of the sedimentation tank are given in Table 5. The results of the sludge treatment will be reported later.

DISCUSSION

Based on the results obtained in this study the following conclusion can be drawn. The suspended and most of the colloidal fractions (in terms of TOC) are efficiently removed from the raw sewage by coagulation–flocculation followed by settling. For ferric chloride, lime and alum the percentage TOC removed of this fractions does not differ much. The percentage reductions have been summarized in Table 6.

A considerable fraction, which is defined as soluble, is removed too. For hydrated lime as coagulant the removal of dissolved organic carbon (DOC) is about 17%. For ferric chloride and alum these percentages are respectively 27 and 24%. In adding ferric chloride as coagulant aid to the flocculation with lime at pH

Table 6. Coagulation–flocculation experiments on pilot-plant scale

			Percentage removal		
Coagulant	Dose	pH	Soluble	Suspended solids	Total
Ferric chloride	61 mg Fe/l	5.3	27	93	54
Hydrated lime	520 mg $Ca(OH)_2$/l	11.0	17	90	44
Alum	47 mg Al/l	5.9	24	94	58

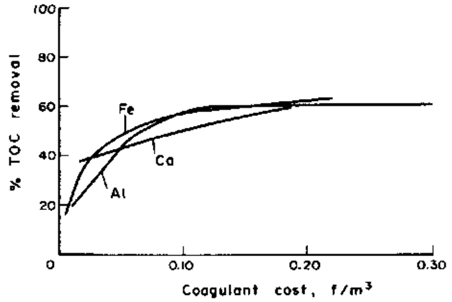

Fig. 8. The coagulant cost per m^3 sewage versus the removal of TOC. Batch experiments.

11.0, the removal percentage of DOC rapidly increases to circa 23%. The resulting effluent of a coagulation–flocculation sedimentation plant consists to a large extent of soluble organics, which are easily biodegradable.

Regarding the coagulant cost in relation to the TOC removal (Fig. 8) the use of iron-III-chloride as coagulant should be favourable. This study indicates that for overloaded conventional mechanical–biological sewage treatment plants a chemical treatment as the first step in a municipal wastewater treatment can be favourable, although the percentage removal is not so high as obtained by other investigators like Cooper & Thomas (1974). This study will be continued with particular attention to this subject.

The results obtained on batch scale and in the small scale pilot-plant with a flow of $0.06\ m^3\ h^{-1}$ are being checked in a larger pilot-plant, having a capacity of $2\ m^3$ sewage h^{-1} and consists of a chemical treatment stage, a multimedia sand-filter and several activated carbon columns.

The chemical treatment stage has been designed as a plug flow reactor with six compartments which are each individually stirred. The experiments with this pilot-plant have been started in October 1975. The results will be published in the future.

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9. COAGULATION-FLOCCULATION OF BEET SUGAR WASTEWATER

J. Leentvaar, H. M. M. Koppers, W. G. Werumeus Buning
Department of Water Pollution Control, Agricultural University,
Wageningen, the Netherlands

The wastewater of the Centrale Suiker Maatschappij (CSM) sugar company at Vierverlaten, Groningen, the Netherlands, consists mainly of water used for hydraulic transportation or "fluming" of sugar beets. Fluming is possible because sugar beets have almost the same density as water; thus the beets are readily carried along by a moving stream.

This means of transportation is not only effective and easy, but also washes away dirt encrusted on the beets. However, it has one disadvantage: some sugar is lost to the flume water by diffusion through the skin of the beet, or, more seriously, from broken beets.[1] In addition to dirt and sugar, the wastewater (total flow of 35 m^3/min) contains other sugar products and excess condensate with a large amount of ammonia (Figure 1). The larger particles are settled in a sedimentation tank; the remaining liquor is cooled and treated in an aerated lagoon. The water is recirculated into the mill; only a portion is discharged. This study investigated coagulation/flocculation of the effluent from the aerated lagoon as a method to permit reuse of this effluent in the sugar mill, or, alternatively, to permit discharge to surface waters.

The following investigations were performed:

- Jar tests with three inorganic coagulants to establish their required doses, pH ranges, and the possible use of coagulation aids;
- Comparison of batch experiments with continuous-flow laboratory experiments and pilot-plant studies; and
- Determination of some design criteria of a coagulation/flocculation plant for sugar mill wastewater.

EXPERIMENTAL SET-UP

Experiments were performed in three ways: on a batch scale, in a laboratory-scale pilot plant, and in a 6-m^3/h pilot plant. The batch coagulation/flocculation tests were done in rectangular 2-l plexiglass tanks with a cross-sectional area of 10 × 10 cm^2. The following test procedure was used:

- Mixing with a turbine stirrer at 660 rev/min, which gave a G-value of about 680/s, measured by means of a torque meter;
- Addition of coagulant solution and then pH-adjustment over a 60-second period at 660 rev/min (rapid mix);
- Flocculation for 30 minutes with a propeller-type stirrer at 67 rev/min (G = 28/s); and
- Sedimentation for 30 minutes.

After sedimentation, a sample of about 100 ml was taken at the half-height of the tank and the sludge volume was measured.

The laboratory-scale flocculator (Figure 2) had a flow of 0.06 m^3/h and consisted of a rapid-mix vessel for coagulant feed and pH-adjustment. This vessel had a volume of 1 litre and was stirred with a turbine-type stirrer at 365 rev/min, which gave a G-value of 150/s. After this initial mixing, the wastewater entered a four-reactor plug-flow flocculator, with a total volume of 20 l. The pH electrode was placed in the first flocculation compartment. The reactors were stirred by a flat-blade stirrer at 63, 50, 22, and 10 rev/min. For technical reasons, the G values were measured at the end of the experimental period; they amounted to 60, 32, 14, and 5/s. Finally the wastewater was allowed to settle in a Dortmund-type sedimentation tank, from which the settled sludge was drawn off con-

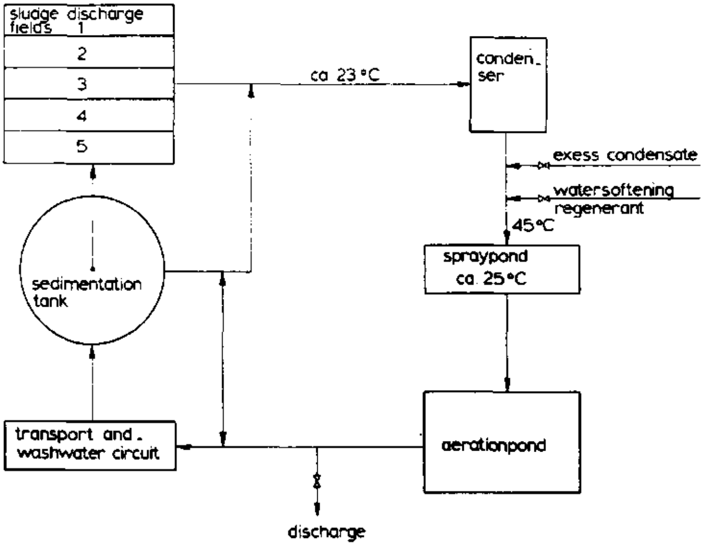

FIGURE 1. Simplified water flow diagram of the sugar mill.

tinuously. The detention time in the tank was 1 hour; the surface loading rate was 0.5 $m^3/m^2 \cdot h$.

The second pilot plant was a circulator-type (Degrémont Holland B. V.) sludge blanket flocculator. In the circulator (Figure 3) wastewater and coagulant are mixed initially in the influent pipe. Flocculation occurs in a conical pipe inside the tank. Polyelectrolytes are added at the overflow of the conical pipe. Flocculation time is governed by influent flow, which ranged from 4 to 8 m^3/h. The volume of the circulator was 5 m^3, and the surface loading was also determined by the wastewater flow according to the following:

Wastewater flow (m^3/h)	Surface loading ($m^3/m^2 \cdot h$)	Detention time (h)
4	2.2	1.25
5	2.7	1.00
6	3.3	0.83
7	3.8	0.71
8	4.4	0.63

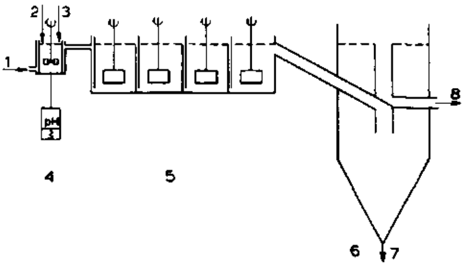

FIGURE 2. The laboratory-scale pilot plant (60 l/h): 1. influent, 2. coagulant dosage, 3. pH adjustment, 4. mixing vessel, 5. flocculator, 6. sedimentation tank, 7. sludge discharge, 8. effluent.

To estimate the settling velocity of the sludge floc, some experiments were carried out in a settling cylinder, with sampling points at different heights. The volume of this cylinder was 0.2 m^3 and the diameter was 0.30 m.

Ferric chloride (40% w/w solution), aluminium sulfate [$Al_2(SO_4)_3 \cdot 18H_2O$] and hydrated lime [$Ca(OH)_2$], were used as coagulants. An anionic, a nonionic, and a cationic synthetic polymer (American Cyanamid Co., Superfloc A100, N100, and C100, respectively) were used as coagulant aids.

RESULTS

Batch experiments. Batch experiments were carried out to determine the ratio of coagulant dose to flocculation effect, the optimal flocculation pH, the effect of addition of coagulant aids, and the amount of sludge produced.

An illustration of the results obtained with ferric chloride in batch experiments is given in Table I. In this table the chemical oxygen demand of the total sample (COD_t) and the

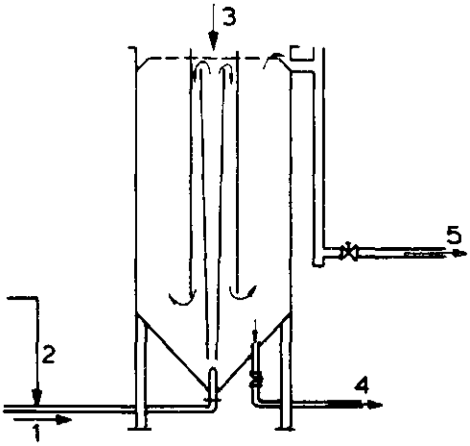

FIGURE 3. **The sludge blanket flocculator (4 to 8 m^3/h): 1. influent, 2. coagulant dosage, 3. coagulant aid dosage, 4. sludge discharge, 5. effluent.**

COD of the supernatant after centrifuging at about 2 500 g for 15 minutes (COD_c) are given with the percentage COD_t reduction at various coagulant doses.

At the start of the working season, the alkalinity of the wastewater was relatively low. During this period, coagulation/flocculation was performed at a pH of at least 5.0 to prevent flotation of flocs by carbon dioxide. Within a few weeks, the alkalinity of the wastewater was so high (about 20 meq HCO_3^-/l) that even at ferric chloride doses up to 250 mg Fe/l, no pH decrease below 5.0 was observed.

TABLE I. **Different ferric chloride doses at different pH values (batch experiments).**[a]

Coagulant Dose (mg Fe/l)	pH	COD_t Reduction (%)	Sludge/ Wastewater (% by-volume)
50	5.5	30	15.0
100	5.5	55	20.0
150	5.5	67	30.0
200	5.5	75	32.0
250	5.5	85	32.0
100	4.0	47	25.0
100	5.0	57	20.0
100	6.0	54	23.0
100	7.0	54	25.0

[a] pH wastewater = 7.8, COD_t wastewater = 1 280 mg O_2/l, and COD_c wastewater = 425 mg O_2/l.

TABLE II. **Effect of coagulant aid on COD reduction and sludge volume for coagulation/flocculation with ferric chloride.**[a]

Coagulant Dose (mg Fe/l)	Coagulant Aid Dose (mg/l A100)	COD_t Reduction (%)	Sludge/ Wastewater (% by volume)
100	—	60	13.5
100	1.0	60	10.5
100	1.5	65	10.0
100	2.0	64	10.0
100	2.5	67	12.5
100	3.0	66	—

[a] pH wastewater = 7.3, pH coagulation = 5.5, COD_t wastewater = 1 010 mg O_2/l, and COD_c wastewater = 500 mg O_2/l.

It turned out that pH had little effect on COD removal in a pH range from 5.0 to 7.0. Table I shows that, depending on the coagulant dose, up to 85% COD_t elimination can be achieved. The experiments showed that the addition of 1 to 2 mg/l anionic polymer A100 with ferric chloride results in an extra COD reduction of about 5% and a reduction of the volume of sludge produced (Table II). The addition of a cationic or a nonionic polymer as coagulant aid had a negligible effect. Several experiments showed that COD removal was maximal when more than 200 mg Fe/l was added.

When alum [$Al_2(SO_4)_3 \cdot 18H_2O$] was used as coagulant, batch experiments showed that the optimal pH for coagulation/flocculation was also higher than 5.0. Table III illustrates that the maximal COD reduction of about 92% occurred at doses higher than 100 mg Al/l. Considerable amounts of sludge were produced. This sludge volume could be reduced by adding 1 to 2 mg/l nonionic polymer N100 as coagulant aid, while anionic and cationic polymers were not so effective (Table IV). Previous coagulation/flocculation experiments with wastewater of domestic origin (Leentvaar *et al.*,[2] Minton and Carlson[3]) showed that, with hydrated lime as a coagulant, the coagulation/flocculation process is determined by the pH, with the understanding that COD removal increases with rising pH. The coagulant can be dosed either up to a fixed pH (for example, pH 11.2) or with a fixed dose. The amount of hydrated lime required for coagulation/flocculation depends on the alkalinity and hardness of the water treated. The experiments with sugar-beet

TABLE III. Different doses of alum at different pH values (batch experiments).[a]

Coagulant Dose (mg Al/l)	pH	$\mathrm{COD_t}$ Reduction (%)	Sludge/ Wastewater (% by volume)
30	5.5	37	4.5
60	5.5	75	17.5
120	5.5	88	37.0
150	5.5	90	42.5
180	5.5	92	50.5
210	5.5	91	57.5
240	5.5	91	66.0
270	5.5	91	80.0
300	5.5	92	85.0
90	4.0	79	10.0
90	5.0	86	25.0
90	6.0	84	27.5
90	7.0	82	24.5

[a] pH wastewater = 7.9, $\mathrm{COD_t}$ wastewater = 1 400 mg O_2/l, and $\mathrm{COD_c}$ wastewater = 425 mg O_2/l.

TABLE V. Hydrated lime as coagulant from batch experiments.[a]

Coagulant Dose [mg $Ca(OH)_2$/l]	pH	$\mathrm{COD_t}$ Reduction (%)	Sludge/ Wastewater (% by volume)
660	9.6	7	—
1 320	11.5	23	4.5
1 980	11.8	54	5.5
2 640	12.0	62	6.0
3 300	12.0	72	9.5
3 960	12.1	75	10.0
4 620	12.0	78	12.0
5 280	12.1	75	12.0
5 940	12.2	75	12.5
6 600	12.2	79	12.0

[a] pH wastewater = 7.6, $\mathrm{COD_t}$ wastewater = 1 240 mg O_2/l, and $\mathrm{COD_c}$ wastewater = 590 mg O_2/l.

wastewater, however, showed (Table V) that pH was not the most important factor in this coagulation/flocculation process. A fixed amount of hydrated lime added to the wastewater gave a higher COD removal percentage, up to 79%, than when a lime dose was added to a fixed pH. This is possibly a result of the low alkalinity of the wastewater at the start of the working season of the sugar mill; therefore, the lime dose per unit volume of wastewater was fixed. Table V shows that COD removal was maximal at lime doses above 2 500 mg $Ca(OH)_2$/l. The addition of organic polymers together with lime had almost no effect on the COD removal and volume of the produced sludge. Addition of small quantities of ferric chloride (about 10 mg Fe/l) with the lime led to a substantial improvement in COD removal, but also to an increase in sludge volume.

TABLE IV. Effect of a nonionic polymer on COD reduction and sludge volume for coagulation/flocculation with alum in batch.[a]

Coagulant Dose (mg Al/l)	Coagulant Aid Dose (mg/l N100)	$\mathrm{COD_t}$ Reduction (%)	Sludge/ Wastewater (% by volume)
100	—	78	58.0
100	1.0	70	51.0
100	2.0	70	36.5
100	3.0	76	30.0
100	4.0	71	26.0
100	5.0	79	26.0

[a] pH wastewater = 7.8, pH coagulation = 5.5, $\mathrm{COD_t}$ wastewater = 1 300 mg O_2/l, and $\mathrm{COD_c}$ wastewater = 330 mg O_2/l.

A disadvantage of lime treatment is the high effluent pH and the increase in the hardness of the treated water. The hardness of the raw wastewater averaged 7.6 meq/l; depending on the lime dose [1 500 to 3 000 mg $Ca(OH)_2$/l], the effluent hardness ranged from 20.5 to 40.3 meq/l. This effluent was thus unfit for recirculation in the sugar mill. However, these disadvantages could be prevented by recarbonation.

As nitrogen plays an important role in the discharge cost for polluted waters into surface water or into the local sewer system, the elimination of organic and inorganic nitrogen compounds was examined incidentally both in batch experiments and in the two pilot plants. All data showed a linear relationship (Figure 4) between COD and Kjeldahl nitrogen removal (Number of data = 17; correlation coefficient $r = 0.88$).

Table VI lists reductions for COD, total organic carbon (TOC), and volatile organic acids by coagulation/flocculation with different doses of ferric chloride, alum, and hydrated lime. The amounts of acetic, propionic, isobutyric, butyric, isovaleric, and valeric acids were determined. The last three compounds played relatively minor roles (concentrations less than 5 mg/l). Table VI shows that volatile organic acids were not removed by coagulation/

TABLE VI. COD and TOC values and the concentration of volatile organic acids after coagulation/flocculation in a batch experiment (7.5 pH wastewater).

Coagulant	Coagulant Dose (mg/l)	COD (mg O_2/l)	TOC (mg C/l)	Volatile Organic Acids[a] C_2 (mg/l)	C_3 (mg/l)	iC_4 (mg/l)
Wastewater		4 610	1 230	250	400	5
Fe	50	3 960	1 070	270	420	5
	150	2 120	595	295	465	7
	250	1 210	450	290	460	4
Al	30	3 640	1 135	250	405	5
	90	1 690	505	315	500	6
	150	1 400	465	280	440	5
$Ca(OH)_2$	1 000	3 670	1 030	310	470	5
	2 000	2 830	920	310	485	6
	3 000	2 160	635	253	410	6

[a] C_2 = acetic acid, C_3 = propionic acid, and iC_4 = isobutyric acid. C_4, iC_5, and C_6 components < 5 mg/l.

flocculation—in fact, the concentration of these acids increased during the treatment. The removal percentage based on COD was somewhat higher than the removal percentage based on TOC.

The wastewater of the beet-sugar mill does not have a constant quality. During the working season, the total COD and the supernatant COD after centrifuging at about 2 500 g (COD$_c$) increased (Figure 5). This COD$_c$ comes from soluble products such as sugars and volatile organic acids and also some colloidal material. It was assumed that the increasing wastewater COD during the working season decreases the COD removal percentage at a fixed coagulant dose. Batch experiments with the three coagulants at fixed coagulant doses, however, showed a constant removal efficiency with respect to COD. The COD$_t$ removal decreased when there was an extra increase in COD$_c$ after a process failure. This extra supply of molasses (COD$_c$) decreased the COD$_t$ removal because this soluble product was not involved in coagulation (Table VII).

Pilot-plant experiments. As mentioned previously, two continuous-flow pilot plants were used: a laboratory-scale plant with a wastewater flow of 0.06 m³/h and a circulator with a flow adjustable from 4 to 8 m³/h. The experiments with the laboratory pilot plant were

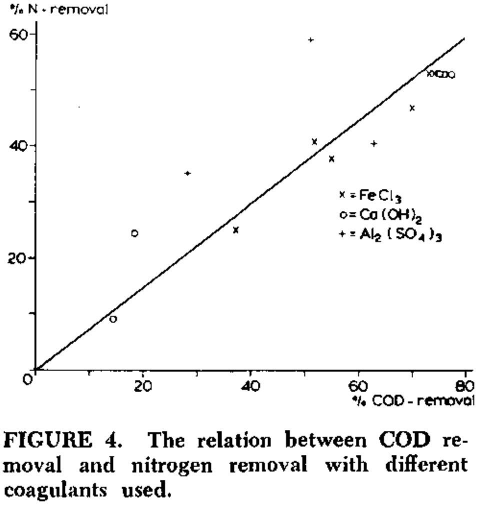

FIGURE 4. The relation between COD removal and nitrogen removal with different coagulants used.

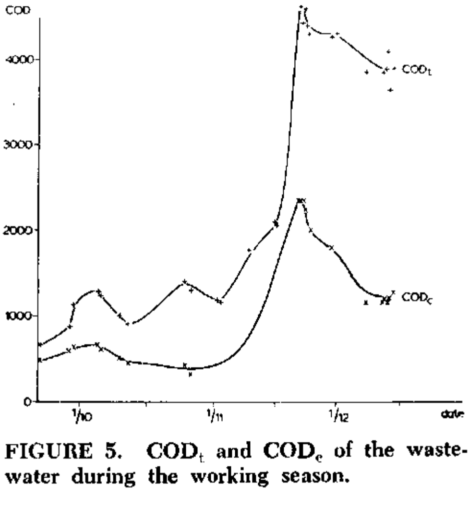

FIGURE 5. COD$_t$ and COD$_c$ of the wastewater during the working season.

TABLE VII. COD reduction before and after the extra supply of molasses to the wastewater.

Coagulant	Coagulant Dose (mg/l)	COD_t reduction percentage	
		Before	After
Fe	50	38	15
	100	60	—
	150	70	51
	250	80	72
Al	30	36	22
	60	75	44
	90	84	64
	150	90	70
$Ca(OH)_2$	1 000	23	12
	2 000	65	31
	3 000	73	47

to determine whether the COD removal percentages of the jar test corresponded with those of the continuous experiments. For this reason, the surface loading of the sedimentation tank was very low: 0.5 $m^3/m^2 \cdot h$. Design criteria were obtained through experiments with the circulator, together with experiments in the sedimentation cylinder. For this reason, the surface loading and, by that, the average detention time of the liquid in the circulator were varied. The experiments were performed with large and small coagulant doses and with a coagulant aid. For coagulation/flocculation with ferric chloride as coagulant, 2.0 mg/l anionic polymer A100 was added; with alum, 2.0 mg/l nonionic polymer N100; and with hydrated lime, 30 mg/l Fe. A synopsis of data of the experiments on batch scale, laboratory scale, and semitechnical scale is given in Table VIII. Other experiments gave the same results.

Figure 6 illustrates that the removal percentages of both laboratory-scale flocculator and circulator corresponded well with those obtained in the jar tests for all three coagulants. The correlation coefficient (r) between the laboratory-scale data and the batch experiments data was 0.92 ($N = 17$) and that between the circulator experimental results

TABLE VIII. Synopsis of data of experiments on bath scale (B), laboratory scale (L), and semitechnical scale (C).[a]

Coagulant	Coagulant Dose (mg/l)	COD_t/COD_c (mg O_2/l)	COD_t Reduction (%)			Surface Loading C (m/h)
			B	L	C	
Fe	50	1 180/495	38	56	39	2.7
	50	1 160/515	48	57	39	2.7
					37	3.8
	200	1 340/375	88	85	92	2.2
					80	3.3
Al	30	2 190/795	51	40	64	2.2
	30	2 070/665	47	45	64	2.2
	30	4 640/2 410	24	30	23	2.2
					28	2.7
	30	4 430/2 350	13	17	20	2.2
					21	3.8
	60	4 390/2 240	46	52	45	2.2
					37	3.8
	60	4 310/2 000	42	56	51	2.2
					28	3.8
	60	4 210/1 790	41	28	49	2.2
					52	3.3
	60	4 320/–	44	53	42	3.8
$Ca(OH)_2$	1 000	3 860/1 170	9	11	10	3.8
	1 000	3 910/1 200	12	11	10	3.8
	1 000	4 100/1 165	14	12	14	3.8
	2 000	3 640/1 200	20	16	24	3.8
	2 000	5 530/1 200	43	47	47	3.8
	2 000	3 890/1 270	25	19	19	4.5

[a] Coagulant aids: Fe, 2.0 mg A100/l; Al, 2.0 mg N100/l; and Ca, 30 mg Fe/l.

and the results of the jar tests was 0.93 ($N = 24$), in which N is the number of experiments.

Design. Because the cost of the sedimentation tank is the most important part of the investment cost, this tank should be designed very carefully. Therefore, the settling velocity of the flocs was measured under different conditions in a vertical settling cylinder, as previously described. The wastewater in the cylinder was flocculated by adding a large or small amount of coagulant together with a coagulant aid and by mixing with a perforated plate. During the settling of the flocs, samples were taken at different heights of the cylinder; from these the COD was determined. As flocculent particles settle, the settling velocity increases with time and depth. In the case of the sedimentation cylinder, efficiency of the sedimentation decreases with the height of the sampling point. An example is given in Figure 7 in which the removal ratio by sedimentation is given as a function of the surface loading for different depths of the sedimentation tank for the case of 1 000 mg $Ca(OH)_2$/l and 30 mg Fe/l as coagulant (aid).

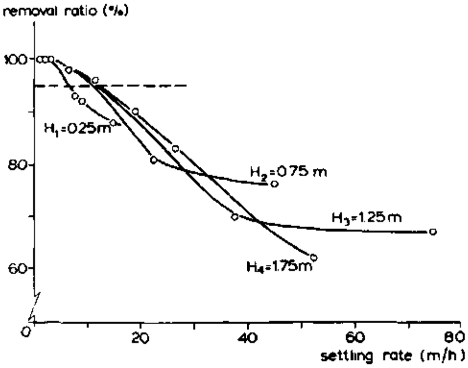

FIGURE 7. Removal ratio by sedimentation as a function of the surface loading/settling rate for different depths (H) of the sedimentation cylinder, for the case of 1 000 mg/l $Ca(OH)_2$ plus 30 mg/l Fe as coagulants.

From these graphs the surface loading of an upflow sedimentation tank with a known depth can be determined at a fixed degree of purification. These values are given in Table IX, which shows that a small coagulant dose led to some flocculent settling and that a high dose led to zone sedimentation (compare 30 and 90 mg Al/l).

Similar settling tests proved that an increase

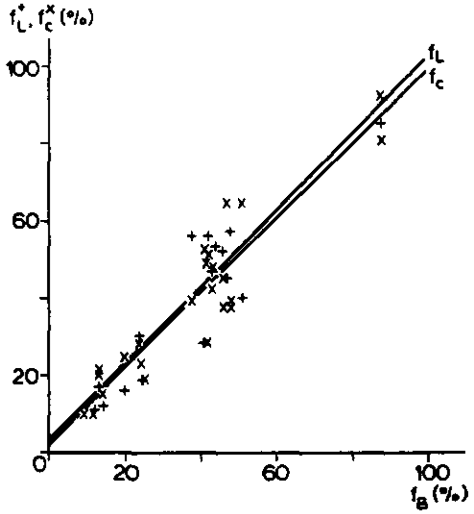

FIGURE 6. Relation between removal percentage of the batch experiments (f_B) and the removal percentage of the laboratory scale (f_L) and the pilot-plant scale (f_C) experiments, based on COD.

TABLE IX. Relation between settling rate (S) and depth of sedimentation tank (H) for different coagulants (removal ratio 95%).

Coagulant Dose	H(m)	S(m/h)
50 mg Fe/l + 2.0 mg A100/l	0.25	8.0
	0.75	8.5
	1.25	10.0
	1.75	8.5
200 mg Fe/l + 2.0 mg A100/l	0.25	0.6
	0.75	3.8
	1.25	4.3
30 mg Al/l + 2.0 mg N100/l	0.25	2.7
	0.75	3.3
	1.25	4.1
	1.75	4.1
90 mg Al/l + 2.0 mg N100/l	0.25	1.4
	0.75	1.6
	1.25	1.7
1 000 mg $Ca(OH)_2$/l + 30 mg Fe/l	0.25	6.5
	0.75	12.0
	1.25	13.0
	1.75	13.0
2 000 mg $Ca(OH)_2$/l + 30 mg Fe/l	0.75	2.4
	1.25	3.2
	1.75	<4.2

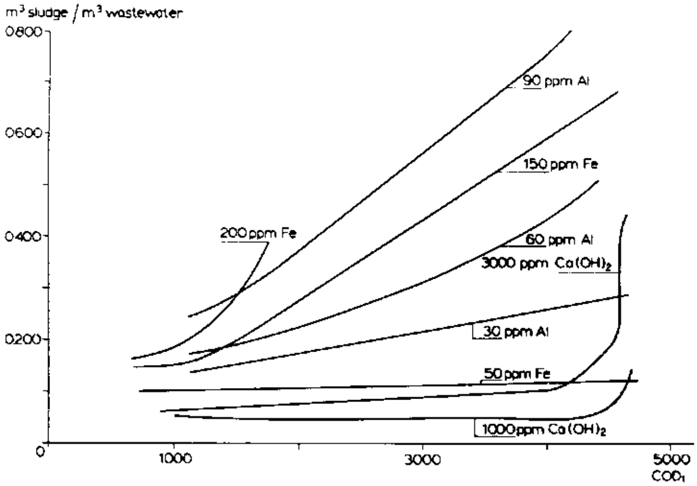

FIGURE 8. Volume sludge produced per m^3 wastewater as a function of wastewater COD and type of coagulant.

of suspended solids in the wastewater had a positive effect on the settling rate: hence a settling rate that is lower at the start of the working season than at the end of the season. The tests also showed that addition of coagulant aids resulted in larger flocs, which settle more rapidly. The results of the tests in the sedimentation cylinder agreed reasonably well with those obtained with the circulator, as illustrated in Table VIII, which shows that in the case of coagulation with 60 mg Al/l, a surface loading of 3.8 m/h was too high for adequate separation of the flocs and the effluent; flocs appeared in the effluent, and the COD removal percentage decreased.

This result corresponded with those of the column settling test (Table IX) at a dose of 90 mg Al/l, in which the settling velocity at a depth of 1.25 m was 1.7 m/h; if the values for the settling velocity at 0.25, 0.75, and 1.25 m are extrapolated, then the sedimentation rate will not be 3.8 m/h or higher at a depth of 3.5 m in the circulator.

Sludge. As illustrated in Figure 8, the amount of sludge produced depends on the COD of the wastewater and the dose and kind of coagulant. The dry solids content of the sludge was 10 g/l with ferric cloride and alum as coagulant and 25 to 30 g/l with coagulation/flocculation by hydrated lime. The volume of the sludge and its dry solids content was measured after 30 minutes of sedimentation. Addition of coagulant aids and sludge recirculation will have a positive effect on the dry solids content of the sludge.

The sludge produced in the physico-chemical treatment has to be transported for about 450 m to be dumped together with solid material from the sugar production on a wastewater field. A jar test was set up to gain an impression of the strength of the sludge floc. Sugar-waste sludge, physico-chemical sludge, and a 5:1 mixture of both sludges was agitated with a velocity gradient of about 200/s for 3 minutes. After 24 hours the COD$_t$ values of the supernatant and the sludge volume were measured and compared with these values before agitation. Table X shows that the agitation of iron sludge led to a 22% increase in COD and also to an increase in the volume of sludge. Alum and lime sludges were very strongly disintegrated by agitation. Agitation of a 5:1 mixture of sugar-waste sludge with iron or lime sludge resulted in an increase of the COD of the supernatant by about 22% and a decrease in sludge volume of 14%.

Agitation of sugar-waste sludge gave an increase in the COD of the supernatant by 5%. As the flow of suspended sugar-waste sludge was 480 m^3/h and the flow of the physico-chemical sludge was in practice 20 m^3/h, the COD percentage increase as a result of the agitation/transportation of this mixture would be less than 5% if the agitation were not higher than 200/s. The G value of 200/s corresponds

TABLE X. Influence of agitation on the release of COD from physico-chemical sludge and sugar waste sludge.[a]

	COD_t Supernatant			Sludge/wastewater (% by volume)		
Sludge Type	Before Agitation ($mg\ O_2/l$)	After Agitation ($mg\ O_2/l$)	Difference (%)	Before Agitation	After Agitation	Difference (%)
Sugar waste sludge	4 650	4 890	(+ 5)	14.0	14.5	(+ 4)
Iron sludge	2 020	2 460	(+ 22)	42.0	46.5	(+11)
Mixture (Fe)	4 400	5 320	(+ 21)	17.5	15.0	(−14)
Alum sludge	2 310	4 900	(+112)	41.0	34.0	(−17)
Mixture (Al)	4 530	6 169	(+ 36)	14.5	12.5	(−14)
Lime sludge	3 680	9 880	(+168)	50.0	42.5	(−15)
Mixture (Ca)	4 660	5 790	(+ 24)	17.5	15.0	(−14)

[a] The COD of the supernatant was measured after 24 hours of sedimentation. The "mixture sludge" consisted of a 5:1 mixture of sugar-waste sludge and physico-chemical sludge.

roughly with a pipe diameter of 0.15 m at a flow of 20 m^3/h.

ECONOMIC ASPECTS

Though the capital cost of a physico-chemical wastewater treatment plant is lower than that of a mechanical/biological plant, the recurring costs of physico-chemical plant are in most cases higher. The recurring costs of the coagulation/flocculation step consist mainly of the cost of the coagulants. The cost given in Table XI for the various doses of coagulant were calculated using the following prices: ferric chloride (40% w/w $FeCl_3$ solution)—\$103.85/metric ton, alum (98% $Al_2(SO_4)_3 \cdot 18\ H_2O$)—\$162.27/metric ton, and lime [98% $Ca(OH)_2$]—\$85.26/metric ton.

Coagulant efficiency is defined as the total

TABLE XI. A survey of the coagulant efficiency and the coagulant cost at different wastewater COD and with different coagulants.

Coagulant	Coagulant Dose (mg/l)	Wastewater COD_t ($mg\ O_2/l$)	Coagulant Efficiency (kg COD removed/kg coagulant)	Coagulant Cost/kg COD Removed (f)
Fe	50	<1 000	4.0– 7.5	0.18–0.34
	50	>2 000	14.0–15.0	0.09–0.10
	100	<1 000	4.0– 6.0	0.23–0.34
	200	<1 000	2.7– 3.6	0.38–0.51
	200	1 000–2 000	3.6– 8.0	0.17–0.38
	250	<1 000	2.5– 3.0	0.46–0.55
	250	>2 000	~13	~0.11
Al	30	<1 000	~15	~0.25
	30	>2 000	15.0–45.0	0.08–0.25
	60	<1 000	~15	~0.25
	60	>2 000	15.0–40.0	0.09–0.25
	90	<1 000	~11	~0.34
	90	>2 000	11.0–25.0	0.15–0.34
	150	<1 000	~7.5	~0.50
	150	>2 000	7.5–20.0	0.19–0.50
$Ca(OH)_2$	1 000	<1 000	~0.4	~0.39
	1 000	>2 000	0.3– 1.0	0.16–0.52
	2 000	<1 000	~0.35	~0.44
	2 000	>2 000	0.6– 1.0	0.16–0.26
	3 000	<1 000	~0.25	~0.26
	3 000	>2 000	0.5– 0.7	0.22–0.31

amount of COD removed per unit coagulant expressed as kg COD/kg coagulant. Table XI surveys coagulant efficiency and coagulant cost of the three coagulants used in this study. This table illustrates that at a certain coagulant dose, coagulant efficiency increases with rising wastewater COD. At a given wastewater COD, the coagulant efficiency decreased with rising coagulant doses after a certain point.

In view of the coagulant cost, the following coagulant dose is recommended: 50 to 100 mg Fe/l, 30 to 60 mg Al/l, or 1 500 to 2 000 mg $Ca(OH)_2$/l. The choice of the coagulant dose at equal cost per kg COD removed depends on the desired effluent quality and/or the sludge handling and disposal facilities.

DISCUSSION

After sedimentation and aeration, the wastewater of the CSM sugar mill Vierverlaten can be coagulated and flocculated easily under normal conditions by any of the three coagulants, ferric chloride, alum, or hydrated lime. The degree of purification depends partly on the ratio of total COD to COD of the supernatant after centrifuging and on the kind and dose of the coagulant. The addition of coagulant aids such as A100 with ferric chloride as coagulant and N100 with alum as coagulant has a positive effect on COD removal, on the settling rate of the flocs produced, and on the volume of the sludge produced.

To minimize the volume of sludge produced, the coagulant dose should not be too large. The experiments proved that batch coagulation/flocculation tests in rectangular tanks can describe the continuous flow experiments very well and are very useful for estimating the coagulation/flocculation process in practice, for surveying the coagulation/flocculation plant, and for determining the optimal coagulant feed. The settling rate of the flocs as determined with the vertical sedimentation tube give a good indication of the surface loading of the vertical flow settling tank that can be applied. The disadvantage of using alum as coagulant is the possibility of sulfate reduction coupled with release of H_2S when the oxygen supply is insufficient. The disadvantage of hydrated lime as coagulant is the high effluent pH together with the severe hardness of the treated water. With respect to the coagulant cost per kg COD removed, the use of ferric chloride as coagulant, especially with small doses, is the most favorable. The settling rate of the flocs with small ferric chloride doses is also favorable.

The successful application of a coagulation/flocculation system also depends on the kind of biological wastewater treatment applied, because the coagulation/flocculation process removes mainly suspended and colloidal material, while soluble, easily biodegradable compounds remain in solution. Recent experiments have shown that coagulation/flocculation, especially in combination with anaerobic biological pretreatment of wastewater, can be successful.[4]

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10. GENERAL SUMMARY

Although coagulation-flocculation processes have been practiced world-wide for almost a century in water treatment, several problems both in the theoretical and in the applied field have not been resolved yet. Especially interpretation of practical results with respect to governing coagulation-flocculation mechanisms, the extrapolation of data from laboratory experiments, and the optimal design of a coagulation-flocculation plant have not been fully elucidated.

The present studies have been carried out to develop a coagulation-flocculation treatment system for raw sewage of medium strength, as part of an advanced wastewater treatment plant and to elucidate some of the mechanisms involved in coagulation-flocculation of wastewater and effluent.

Chapter 2 describes a simple method to measure the power input by an impeller in a vessel. There are many studies on impeller power dissipation in cylindrical vessels, with or without baffles and only a few on power dissipation in the square tanks used in practice. The experiments showed that the dimensionless Power number for square tanks can be estimated quite well using the Power number of a cylindrical, baffled tank provided with 4 radially placed baffles with a distance between two opposite baffles equal to the diameter of the square tank. Differences between the results of coagulation-flocculation experiments with different tanks and stirrers at equal power imput are probably due to a difference in distribution of energy different tipspeeds of the impellers studied.

Chapter 3 deals with the strength of ferric hydroxide flocs. Floc size was determined by taking pictures of the flocs under agitation. The experiments showed that the addition of a coagulant aid increases floc strength. Other conclusions from these experiments were that floc break up takes place by erosion of small particles from the exterior surface layers of the flocs and not by fracture of flocs and that once disrupted flocs do not grow again.

Chapter 4 gives a report of a modification of an equation for the kinetics of flocculation. The suggestion is made to use the floc volume fraction in flocculation rate expressions instead of the particle concentration.

Chapter 5 describes coagulation-flocculation studies of sewage with lime in order to indentify and quantify the organic matter (TOC) fraction removed by magnesium hydroxide precipitation and the fraction removed due to calcium carbonate precipitation. The relation between removal of TOC and $Mg(OH)_2$ precipitation showed a behaviour similar to that of an adsorption process.

Chapter 6 gives a report on the optimalization of coagulant dose in coagulation-flocculation of sewage. Experiments showed that it is possible to estimate the required coagulant dose from the sewage characteristics. A comparison between a constant coagulant dose (as also applied in previous experiments) and a dose related to the ortho-phosphate concentration of the sewage leads to equal removal with respect to TOC and resulted in a coagulant reduction of 35%. This method of calculating coagulant dose in relation to characteristic sewage parameters is of great economic importance, especially for coagulation-flocculation plants, connected to a combined sewerage system.

Chapter 7 deals with some design criteria for a coagulation-flocculation plant for sewage. The study shows that it is not disadvantageous to use only two flocculator chambers with downward tapered velocity of the impellers. The design criteria of the horizontal flow sedimentation tank only could be obtained in pilot plant experiments. The maximum surface loading in the pilot plant was 1.5 m h^{-1}, with an average detention time of about 50 minutes in a sedimentation tank with a depth of 1.8 m.

In chapter 8 a comparison is made of the effects of different coagulants on the removal of TOC and of some specific compounds from the treated sewage in a small pilot plant and in batch experiments. The experiments showed that the effluent of a coagulation-flocculation plant for raw sewage consists to a large extent of soluble, easily biodegradable organics.

Chapter 9 shows that the application of the coagulation-flocculation process on wastewater of a sugar mill is very promising but that the succesful application of such a system also depends on the kind of biological wastewater treatment applied in conjunction with the physical-chemical plant.

This also applies for the treatment of raw sewage, as coagulation-flocculation, even if followed by sand filtration and active carbon adsorption removes the easily biodegradable compounds very poorly.

Mere coagulation-flocculation can be applied succesfully to some (industrial) wastewaters containing a high amount of suspended solids, heavy metals or phosphorus.

SAMENVATTING

Al sinds eeuwen heeft men gebruik gemaakt van destabilisatie- en vlokvormingsprocessen om troebel water te klaren. Zo werden lang geleden in Egypte gemalen amandelen, in India noten en in China aluin met het water gemengd, waarna de gevormde vlokken in eenvoudige bakken werden bezonken. Het bovenstaande heldere water was dan geschikt om gedronken te worden.

Ook in de begin jaren van de waterzuiveringstechnologie werden vlokmiddelen aan het afvalwater toegevoegd ten einde het water te zuiveren. Dit proces van afvalwaterbehandeling is in het begin van de twintigste eeuw echter verlaten, omdat door middel van deze fysisch-chemische methode voornamelijk gesuspendeerde en kolloïdale stoffen worden verwijderd, terwijl opgeloste, biologisch gemakkelijk afbreekbare stoffen niet, of slechts zeer ten dele uit het afvalwater worden verwijderd. Langzamerhand blijkt echter dat mechanisch-biologische zuivering van afvalwater niet in alle gevallen voldoende is en voegt men soms een fysisch-chemische stap toe ten einde bv. fosfor, zware metalen en/of biologisch moeilijk afbreekbare stoffen te verwijderen.

Het in dit proefschrift beschreven onderzoek is in eerste instantie uitgevoerd als onderdeel van een uitgebreide studie naar geavanceerde zuiveringstechnieken, waarbij het destabilisatie-, vlokvormings- en sedimentatieproces vooraf ging aan zandfiltratie en actieve kool behandeling. Dit onderzoek is echter geleidelijk uitgegroeid tot een meer algemene studie naar de destabilisatie- en vlokvormingsprocessen voor zowel afvalwater als effluent (het biologisch gezuiverde afvalwater). Tevens zijn enkele voor de praktijk relevante fundamentele aspecten onderzocht, ten einde de resultaten ook te kunnen toepassen bij o.a. de drinkwaterproduktie.

Het mengen van vlokmiddelen met het te behandelen water en het daarna roeren van de suspensie om de vlokvorming te bevorderen dient met een bepaalde intensiteit te geschieden. Ten einde de door het roerblad afgegeven energie aan het water te bepalen bij verschillende vormen van bak en roerder zijn experimenten uitgevoerd, die in hoofdstuk 2 zijn beschreven. Uit de literatuur zijn gegevens bekend over ronde bakken met en zonder keerschotten; er zijn echter vrijwel geen gegevens bekend over rechthoekige vaten, die in de praktijk veelal worden gebruikt. Dit onderzoek toonde aan, dat voor praktische toepassing het vermogenskengetal van een gegeven roerder in een

bak met een vierkant grondvlak goed benaderd wordt door het vermogenskengetal van deze roerder in een ronde bak met vier radiaal opgestelde keerschotten, waarbij de afstand tussen twee tegenoverstaande keerschotten gelijk is aan de ribbe van het grondvlak van de vierkante bak. Daarnaast wordt in dit hoofdstuk beschreven, dat bij gelijke energiedissipatie voor verschillende roerders in een bak het zuiveringsrendement van de destabilisatie-vlokvorming verschillend is als gevolg van lokale turbulentie effekten.

Voor de dimensionering van installaties voor de destabilisatie en vlokvorming is kennis van de kinetiek van het vlokvormingsproces en van de sterkte van de vlok noodzakelijk. In hoofdstuk 3 wordt het onderzoek naar de sterkte van de gevormde ijzerhydroxide vlokken beschreven. Uit de proeven is gebleken, dat vlokken, gevormd in aanwezigheid van een vlokhulpmiddel (een anionogeen polymeer) sterker zijn dan vlokken die alleen met ijzer-III-chloride als vlokmiddel zijn gevormd. Voorts is aangetoond, dat het afnemen van de vlokgrootte door intensief roeren geen gevolg is van het breken van vlokken doch van erosie van kleine deeltjes van het vlokoppervlak. Tevens is gebleken, dat een eenmaal kapot geslagen vlok niet meer aangroeit.

Met betrekking tot de kinetiek van de vlokvorming, zoals beschreven in hoofdstuk 4, is een bestaande formule voor de vlokgroei aangepast en uitgebreid.

Het onderzoek naar de destabilisatie-vlokvorming met kalk als vlokmiddel in aanwezigheid van magnesium-ionen in het water (hoofdstuk 5) heeft aangetoond, dat de relatie tussen de verwijdering van organische stof en de magnesiumhydroxide precipitatie sterk lijkt op de relatie die geldt voor een adsorptieproces.

De bedrijfskosten van een destabilisatie-vlokvormingsproces kunnen sterk worden gereduceerd door de vlokmiddeldosering aan de wisselende samenstelling van het afvalwater aan te passen. In hoofdstuk 6 is dit beschreven en de studies hebben aangetoond, dat het ortho-fosfaat gehalte van het afvalwater een goede stuurparameter is voor de vlokmiddeldosering. Door een aangepaste dosering kan een besparing van 35% aan vlokmiddel worden bereikt.

Hoofdstuk 7 handelt over de dimensioneringsgrondslagen voor een installatie, die gebaseerd is op destabilisatie-vlokvorming gevolgd door sedimentatie. Bij dit onderzoek is aandacht besteed aan de verblijftijd in de vlokvormingstank en in het sedimentatiebassin. Ook het effect van een vlokkendeken is onderzocht. Dit onderzoek is uitgevoerd met behulp van ladingsgewijze experimenten en in twee proefinstallaties met een capaciteit van 2 m^3h^{-1}. Het onderzoek toonde aan, dat het mogelijk is om met twee, in plaats van de oorspronkelijke zes, vlokvormingscompartimenten te volstaan. De maximum oppervlaktebelasting van de horizontaal doorstroomde bezinktank is bepaald op 1,5 m h^{-1} bij een gemiddelde verblijftijd van 50 minuten in de 1,8 m diepe tank.

In hoofdstuk 8 worden experimenten beschreven, die zijn uitgevoerd met huishoudelijk afvalwater in een kleine proefinstallatie met een capaciteit van 60 l h^{-1} en met ladingsgewijze experimenten. Bij deze proeven zijn ijzer-III-chloride, aluminiumsulfaat en kalk als vlokmiddelen vergeleken en is de verwijdering van enkele specifieke verbindingen bestudeerd.

In hoofdstuk 9 wordt aangetoond, dat het destabilisatie-vlokvormingsproces toegepast op een afvalwater dat zeer veel gesuspendeerd, doch moeilijk bezinkbaar materiaal bevat zeer goede resultaten afwerpt. Het rendement van de chemische behandeling van het zwemwater van een suikerfabriek met een van de vlokmiddelen ijzer-III-chloride, aluminiumsulfaat of kalk hangt o.a. af van de fractie opgeloste organische stof, de aard en dosis van het vlokmiddel en het eventueel toevoegen van een vlokhulpmiddel.

Het destabilisatie-vlokvormingsproces voor de behandeling van afvalwater verwijdert voornamelijk het gesuspendeerde en kolloïdale materiaal, terwijl opgeloste, gemakkelijk biodegradeerbare stoffen met het effluent worden afgevoerd, zelfs indien na dit proces zandfiltratie en actieve kool behandeling plaatsvinden. Een biologische zuiveringsstap blijft dan ook nodig om de laatstgenoemde bestanddelen te verwijderen.

Voor bepaalde industriële afvalwateren, voor de verwijdering van fosfor, moeilijk biodegradeerbare stoffen en/of zware metalen en voor het opvangen van pieken in de belasting (bv. tijdens het toeristenseizoen) kan fysisch-chemische zuivering en met name het destabilisatie-vlokvormingsproces van grote betekenis zijn.

CURRICULUM VITAE

De auteur werd op 31 december 1948 geboren te Nijmegen. Na het behalen in 1966 van het HBS-B diploma aan het Nijmeegs Lyceum, werd in datzelfde jaar begonnen met de studie in de richting Waterzuivering aan de Landbouwhogeschool te Wageningen. Het doctoraalexamen, afgelegd in 1972, omvatte de vakken waterzuivering, microbiologie, fysische en kolloïdchemie en algemene en sociale gezondheidszorg. Van 1972 tot begin 1979 was hij als wetenschappelijk medewerker verbonden aan de vakgroep Waterzuivering van de Landbouwhogeschool. Gedurende deze periode was de auteur tevens studiecoördinator van de studierichting Milieuhygiëne. In februari 1979 is hij in dienst getreden bij de Deltadienst van de Rijkswaterstaat, hoofdafdeling Milieu en Inrichting te Middelburg en vervult daar de functie van hoofd van de onderafdeling Water-Fysica, tevens plaatsvervangend hoofd van de afdeling Water.