

Cationic polymers in water treatment

Part 1: Treatability of water with cationic polymers

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Abstract

This paper investigates the best attainable treatability to which a water polluted with a technologically significant concentration of organic matter is treatable by different cation-active polyelectrolytes and their blends with mineral coagulants in comparison to that attainable by traditional hydrolysing coagulants. The negative influence of these reagents used as primary coagulants on the treated water quality is demonstrated in the case of Saulspoort Waterworks.

Introduction

One of the prime objectives of water treatment is the removal of colloidal impurities of which organic matter is the most important. It should be emphasised that impurities of an organic nature are far more objectionable from a hygienic point of view than impurities of a mineral nature. Since organic matter can be precursors of organohalogens (carcinogens)(Hocman, 1986), water treatment technology design should always be aimed at achieving the maximum possible removal of organic matter (Polasek and Mangeot, 1988).

The substitution of traditional hydrolysing reagents by cationic polymers (CPE) is becoming increasingly popular in South Africa, although no comprehensive investigation into the suitability of CPE as primary coagulants and their possible side-effects has been carried out. The decision to substitute hydrolysing reagent with CPE is usually based on a simple comparison of reagent dosage costs. Another reason used is that CPE are more user-friendly, i.e. do not change water pH and are easier to handle.

There is relatively little information available in literature on the use of CPE as the primary coagulant and their effect of the final quality of treated water. Some information on this topic can be found in foreign articles (Narkis and Rebhun, 1977; Glazer and Edzwald, 1979; Amy and Chadik, 1983; Carns and Parker, 1985; Tanaka and Pirbazari, 1986; Aizawa et al., 1990; Gregory and Lee, 1990;) and only limited information is available in local articles (Healey et al., 1987; Nozaick et al., 2000a and Nozaick et al., 2000b; Pryor and Freese, 1999; Polasek and Mutl, 2000).

The authors have tested different CPE over many years at different localities in South Africa and verified the suitability of their application on some of the localities where CPE are in use (Polasek and Mutl, 1995b; Mutl and Polasek, 1996; Polasek and Mutl, 1997; Polasek and Mutl, 1999). A comprehensive investigation into the treatability of water attainable with different CPE was carried out at Saulspoort Waterworks during 1993. The objective of this study was to establish the feasibility of using CPE for the treatment of water with a technologically significant organic content. The results obtained are presented in this paper. Part 1 of this article

investigates the influence of CPE on the attainable treatability of water. Part 2 of the article investigates the influence of CPE-formed suspension on the performance of filters.

Significance of organic pollution

The most important organic pollution is produced by humic matter. Humic matter is the most significant precursor of organohalogens and other chlorine-derivates. Therefore, their presence in drinking water is undesirable. In natural waters humic matter occurs, depending on pH value, as negatively-charged macromolecules. The negative charge is caused by the presence of carboxyl and phenolic groups (-COOH and -OH). Both groups dissociate in an alkaline pH range in which humic acids dissolve readily. In an acidic pH range, humic acids do not dissociate and are poorly soluble. Therefore, they can only have a negative charge, the value of which decreases with a decreasing pH value. In surface waters, mixtures of different molecular and micellar colloids exist. Therefore, a compromise operational reaction pH, at which the highest removal of organic impurities is achieved, together with operational dosage of primary coagulants are investigated by jar tests. Most organic impurities contained in water have an acidic character. Therefore, as a rule, the surface waters should be treated in an acidic pH range (Tucek et al., 1977).

The humic matter occurring in low molecular form cannot be removed from water by current chemical treatment (Pitter, 1981). Their removal necessitates the use of advanced treatment processes such as ozonation and activated carbon adsorption.

Testing site

The Saulspoort Waterworks belongs to the Municipality of Bethlehem. The source of raw water is the Saulspoort Dam fed by the Axel River and the Liebenberg Vlei, and is one of the most polluted waters in South Africa. Its turbidity fluctuates considerably throughout the year while organic pollution, characterised by a COD_{Mn} value, is relatively high but fairly steady, varying between $COD_{Mn} = 5$ to $7 \text{ mgO}_2 \cdot \text{L}^{-1}$. For raw water data see Table 1.

The design capacity of the Saulspoort Waterworks is 40 Ml/d . The treatment process is based on a two-stage separation of the formed suspension. The flocculent suspension is formed under conditions of the Inline High Density Suspension (IHDS) process

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Determinant	Unit	Maximum	Minimum
pH	[-]	8.2	7.4
Colour	[HU]	40	10
Turbidity	[NTU]	250	20
Total Alkalinity	[mg CaCO ₃ ·ℓ ⁻¹]	160	90
Fe	[mg·ℓ ⁻¹]	1.5	0.5
COD _{Mn}	[mg O ₂ ·ℓ ⁻¹]	6.5 to 5.9 *	

* measured at the time of testing

(Polasek and Mutl, 1995a; Polasek, 1970 and 1972). The formed suspension is first separated in a High Rate (HR) sludge blanket clarifier followed by filtration in rapid gravity dual media filters. The first separation process unit consists of four HR clarifiers, each of a diameter $D_{CL} = 8.65$ m. The HR clarifier incorporates flocculation, sludge blanket, treated water and sludge thickening compartments. No lamella or similar facility forms part of the clarifier design. Each clarifier with a capacity $Q = 10$ Mℓ/d, is designed for an upflow velocity $v_{SB} = 11$ m/h at the sludge blanket level. It was successfully tested at 50% hydraulic overload. The removed sludge is first thickened in the sludge compartment up to 75 g·ℓ⁻¹ (Polasek and van Duuren, 1981) prior to its discharge from the clarifier for further dewatering. The second separation process unit, filtration, consists of eight dual media filters, each designed for a filtration velocity of $v_F = 10$ m/h. At the time of testing, CPE L-100 was used at the waterworks as the coagulant.

Jar tests and their evaluation

The treatment process efficiency attainable by different CPE was investigated by jar tests. CPE, both natural and synthetic, and commercially available blended CPE were tested. The CPE of synthetic origin were represented by polyamine and polydiallyldimethylammonium chloride (polyDADMAC) - probably the most widely used cationic polyelectrolyte in water treatment today. The CPE of natural origin was represented by Belfloc, a blend of Floccotan (a partially condensed product of commercial wattle tannin extract treated to produce active amine groups along the polymerised molecule) and polyDADMAC.

In order to obtain a reference datum to which treatability of the water obtained with CPE could be compared, traditionally used hydrolysing reagents, namely ferric chloride and aluminium sulphate, together with polyaluminium chloride (PACl), were also tested.

The unwillingness of the CPE suppliers to provide technical specifications and basic information about their products which are important from the treatment process point of view made the evaluation of the efficiency of the treatment process considerably more difficult. Due to a lack of available information, the composition of the CPE tested had to be assessed. This assessment is based on the sketchy information obtained from different sources and the results of analysis obtained during testing.

The standard jar test operation and testing procedures adopted in this study are in accordance with the Guidelines to coagulation and flocculation for surface waters (Polasek P and Mutl S 1995). All jar tests were carried out under the conditions of the IHDS process with 5 min rapid agitation at $\bar{G} = 200$ s⁻¹ followed by 10 min

Determinant	DOC [mg C·ℓ ⁻¹]	TOH _p [mg CHCl ₃ ·ℓ ⁻¹]
Raw water	5.2	878
Flocculated water	4.8	1211
Filtered water	4.6	1209

slow agitation at $\bar{G} \approx 30$ s⁻¹.

The attainable treatability of the water was evaluated against the following three pollution determinants:

- cation of added hydrolysing reagent Me (Fe or Al) introduced into the water by the dosed coagulant,
- organic pollution characterised by COD_{Mn} value, determined by the Kubel method (Kubel, 1866), and measured in accordance with the method described in Polasek and Mutl, 1995a and
- turbidity (Tu).

The reaction pH was also monitored.

The methodology of sampling, analytical processing of samples and evaluation of the results obtained can be found in Guidelines to coagulation and flocculation for surface waters (Polasek and Mutl, 1995a). The Tu₆₀F and Me₆₀F are the residual turbidity and the concentration of cation of added hydrolysing reagent caused by their respective non-separable particles remaining in the treated water. They were measured in a sample of treated water taken after 1h sedimentation from which the separable particles were removed by centrifugation. The Tu₆₀F value represents the actual quality to which water is treated with respect to turbidity by the treatment processes applied. The Me₆₀F value represents the overall capability of the treatment process with respect to the formation of separable suspension.

The COD_{Mn60} value expresses the total concentration of organic matter remaining in the treated water. It is measured in a sample of treated water taken after 1h sedimentation. The COD_{Mn60} value indicates the quality to which water is treatable with respect to organic pollution.

The ϕ_{COD} expresses the separation efficiency of the treatment process with respect to organic pollution. It is a ratio of the content of organic pollution separated in the treatment process and its total initial content in the raw water. It is used for comparison of the treatment efficiency achieved by individual reagents.

An important part in evaluating the treatment process efficiency of individual coagulants from an operational point of view is their coagulant dosage cost. Because the water could not be treated to the same quality by all coagulants tested, the coagulant dosage cost was established for the operational dosage D_o at which the most effective reduction of all pollution determinants used was achieved. The dosage cost was calculated by multiplying the operational dosage by the coagulant price. It should be emphasised that when comparing the coagulant dosage costs, it is necessary to also take into consideration the quality of water and the quality to which it is treatable by the coagulant.

The optimum dosage means the dosage by which maximum

reduction in the content of a pollution determinant monitored, is achieved. The operational dosage means the dosage at which the maximum possible removal of all types of impurities is achieved.

The investigation into the treatability of surface waters carried out during 1993 showed that most of the surface waters in South Africa are easily treatable to a high quality under optimum reaction conditions by the common treatment processes utilising hydrolysing reagents (Polasek and Mutl, 1995a; Polasek and Mutl, 1995b; Mutl and Polasek, 1996; Polasek and Mutl, 1997; Polasek and Mutl, 1999). These wholesome water quality limits to which the treatability of water attainable by the coagulants tested are compared, are as follows:

- cation of added hydrolysing reagent used $Me = 0.15 \text{ mg}\cdot\text{L}^{-1}$ and in many cases $Me < 0.05 \text{ mg}\cdot\text{L}^{-1}$,
- organic matter characterised by $\text{COD}_{\text{Mn}} = 2.0 \text{ mg O}_2\cdot\text{L}^{-1}$,
- mineral suspensions producing turbidity $Tu = 0.3 \text{ NTU}$.

When evaluating the potential of any CPE as a suitable substitute for hydrolysing reagents, the quality to which the water is treatable by CPE should be within the above limits. The reason for setting these limits, rather than referring to the limits specified in South African standard stated below, is that the range of the maximum limits allowed for in the SABS 241/99 for the respective pollution determinants are far too lax for a wholesome quality drinking water:

- cation of added hydrolysing reagent used $Me = 0.15$ to $0.5 \text{ mg Al}\cdot\text{L}^{-1}$ and $Me = 0.1$ to $2.0 \text{ mg Fe}\cdot\text{L}^{-1}$,
- organic pollution characterized by $\text{DOC} = 5$ to $20 \text{ mg C}\cdot\text{L}^{-1}$ and $\text{TOH}_T = 100$ to $300 \mu\text{g CHCl}_3\cdot\text{L}^{-1}$,
- turbidity $Tu = 1$ to 10 NTU .

The term “water treatment” is used in this article in the commonly accepted context of “water purification”.

Hydrolysing reagents

The treatability of the water attainable by hydrolysing reagents namely, FeCl_3 , $\text{Al}_2(\text{SO}_4)_3$ and PACl (M-30, K-288), is shown in Figures 1 to 4. These Figures illustrate the dependence of changes of the pollution determinants on dosage. The treated water qualities obtained are summarised in Table 3.

Ferric chloride

The range of ferric chloride dosages applied was designed to almost deplete alkalinity of the water by hydrolysis. The dosages applied covered a range $D = 6$ to $135 \text{ mg}\cdot\text{L}^{-1}$. The results obtained are plotted in Fig. 1.

As can be seen from Fig. 1, the residual content of Fe is very low over the full range of dosages applied. The lowest residual Fe value, $Me_{60}F = 0.01 \text{ mg Fe}\cdot\text{L}^{-1}$, was obtained at a dosage $D = 74 \text{ mg}\cdot\text{L}^{-1}$. Turbidity dropped rapidly up to breakpoint at a dosage $D = 50 \text{ mg}\cdot\text{L}^{-1}$ and, thereafter, gradually decreased at a much lower rate. The lowest residual turbidity, $Tu_{60}F = 0.12 \text{ NTU}$, was obtained at a dosage $D = 123 \text{ mg}\cdot\text{L}^{-1}$. This dosage can be considered to be the optimum dosage for destabilisation of turbidity particles. Sufficient aggregation efficiency of turbidity particles was achieved at a dosage $D = 65 \text{ mg}\cdot\text{L}^{-1}$. The COD_{Mn} value decreased over the full range of dosages applied. It dropped fairly rapidly to breakpoint at a dosage $D = 110 \text{ mg}\cdot\text{L}^{-1}$ and, thereafter, its drop was considerably smaller. The lowest $\text{COD}_{\text{Mn}60} = 1.19 \text{ mg O}_2\cdot\text{L}^{-1}$ was obtained at the

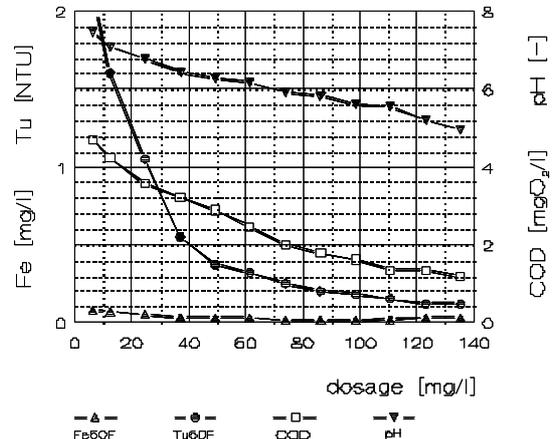


Figure 1
Treatment process efficiency attainable with FeCl_3

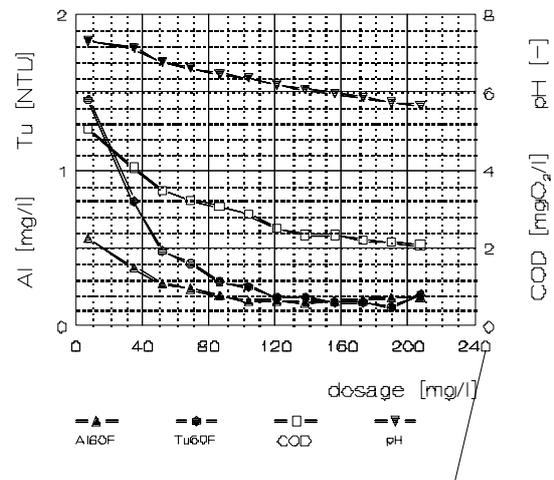


Figure 2
Treatment process efficiency attainable with $\text{Al}_2(\text{SO}_4)_3$

maximum dosage applied, $D = 136 \text{ mg}\cdot\text{L}^{-1}$. The reaction pH value dropped gradually with dosage from $\text{pH} = 7.46$ to 4.96 at the maximum dosage.

Based on the evaluation of the results obtained with respect to all three pollution determinants, a dosage $D = 75 \text{ mg}\cdot\text{L}^{-1}$ is considered to be the optimum operational dosage at which wholesome quality water is produced; the reaction $\text{pH} = 6.0$.

Aluminium sulphate

Due to high alkalinity and concentration of organic matter, aluminium sulphate was tested over a wide range of dosage, $D = 7$ to $207 \text{ mg}\cdot\text{L}^{-1}$. The results obtained are plotted in Fig. 2.

Figure 2 shows that the residual content of Al decreases rapidly up to a dosage $D = 86 \text{ mg}\cdot\text{L}^{-1}$ and, thereafter, decreased at a gradually diminishing rate up to a dosage $D = 140 \text{ mg}\cdot\text{L}^{-1}$. At higher dosages it remained almost unchanged. The lowest residual Al value, $Me_{60}F = 0.15 \text{ mg Al}\cdot\text{L}^{-1}$, was obtained at a dosage $D = 138 \text{ mg}\cdot\text{L}^{-1}$. Therefore, this dosage can be considered to be the optimum dosage of the treatment process with respect to the formation of separable suspensions. Turbidity dropped rapidly up to breakpoint at a dosage $D = 50 \text{ mg}\cdot\text{L}^{-1}$ and, thereafter, dropped at a much lower rate. The lowest residual turbidity, $Tu_{60}F = 0.12 \text{ NTU}$, was obtained at a dosage $D = 190 \text{ mg}\cdot\text{L}^{-1}$. Therefore, this dosage is considered to be

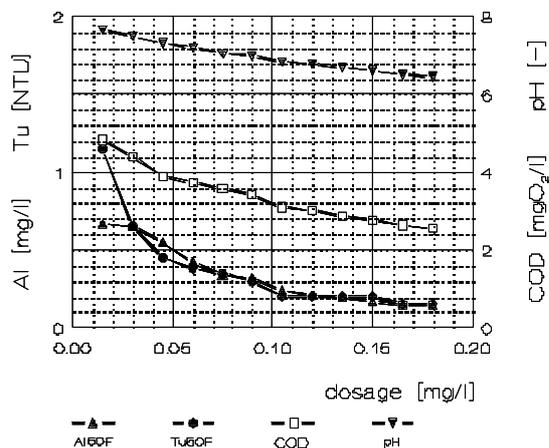


Figure 3

Treatment process efficiency attainable with PACI. Product M-30.

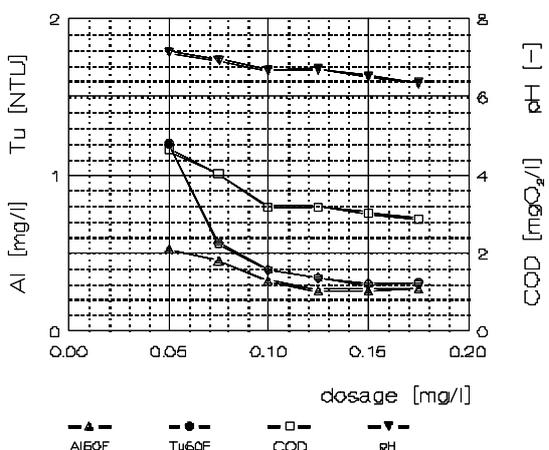


Figure 4

Treatment process efficiency attainable with PACI. Product K-288.

the optimum dosage for destabilisation of turbidity particles. Sufficient aggregation efficiency of turbidity particles was achieved at a dosage $D = 86 \text{ mg} \cdot \text{l}^{-1}$. The COD_{Mn} value continuously decreased over the full range of dosages tested. From a dosage $D = 138 \text{ mg} \cdot \text{l}^{-1}$ the rate of decrease in COD_{Mn} value is reduced considerably. The lowest $\text{COD}_{\text{Mn}60} = 2.08 \text{ mg O}_2 \cdot \text{l}^{-1}$ was obtained at the maximum dosage applied, $D = 207 \text{ mg} \cdot \text{l}^{-1}$. The reaction pH value dropped gradually with dosage from $\text{pH} = 7.32$ to 5.67 at the maximum dosage.

Based on the evaluation of the results obtained with respect to all three pollution determinants, a dosage $D = 38 \text{ mg} \cdot \text{l}^{-1}$ is considered to be the operational dosage; the reaction $\text{pH} = 6.2$. Wholesome quality water was not produced due to slightly higher COD_{Mn} value.

Polyaluminium chloride

Two PACI products, namely M-30 and K-288, produced by two different manufacturers, were tested. The range of PACI dosages tested was designed to correspond to the range of Al concentration applied with aluminium sulphate. The results obtained are plotted in Figs. 3 and 4.

M-30

Figure 3 shows that the residual Al content gradually decreased over the full range of dosage applied. The lowest residual Al value, $\text{Me}_{60}\text{F} = 0.14 \text{ mg Al} \cdot \text{l}^{-1}$, was obtained at a dosage $D = 0.180 \text{ ml} \cdot \text{l}^{-1}$. This dosage can be considered to be the optimum dosage of the treatment process with respect to the formation of separable suspensions. The maximum permissible concentration of residual Al ($\text{Me}_{60}\text{F} = 0.15 \text{ mg Al} \cdot \text{l}^{-1}$) was obtained at a dosage $D = 0.165 \text{ ml} \cdot \text{l}^{-1}$. Turbidity dropped rapidly up to breakpoint at a dosage $D = 0.045 \text{ ml} \cdot \text{l}^{-1}$ and, thereafter, dropped at a much lower rate. The lowest residual turbidity, $\text{Tu}_{60}\text{F} = 0.15 \text{ NTU}$, as obtained at a dosage $D = 0.165 \text{ ml} \cdot \text{l}^{-1}$. Therefore, this dosage can be considered to be the optimum dosage for destabilisation of turbidity particles. Sufficient aggregation efficiency of turbidity particles was achieved at a dosage $D = 0.090 \text{ ml} \cdot \text{l}^{-1}$. The COD_{Mn} value gradually decreased over the full range of dosages tested. The lowest residual $\text{COD}_{\text{Mn}60} = 2.55 \text{ mg O}_2 \cdot \text{l}^{-1}$ was obtained at the maximum dosage applied, $D = 0.180 \text{ ml} \cdot \text{l}^{-1}$. The reaction pH value dropped gradually with dosage from $\text{pH} = 7.67$ to 6.45 at the maximum dosage.

Based on the evaluation of the results obtained with respect to all three pollution determinants, a dosage $D = 0.165 \text{ ml} \cdot \text{l}^{-1}$ is considered to be the operational dosage; the reaction $\text{pH} = 6.5$. Wholesome quality water was not produced due to higher COD_{Mn} value.

K-288

Figure 4 shows that the residual content of Al gradually decreased up to a dosage $D = 0.125 \text{ ml} \cdot \text{l}^{-1}$ and thereafter remained almost unchanged. The lowest residual Al value, $\text{Me}_{60}\text{F} = 0.26 \text{ mg Al} \cdot \text{l}^{-1}$, was obtained at this dosage, which is considerably higher than the maximum permissible concentration $\text{Me}_{60}\text{F} = 0.15 \text{ mg Al} \cdot \text{l}^{-1}$. Turbidity dropped rapidly up to breakpoint at a dosage $D = 0.100 \text{ ml} \cdot \text{l}^{-1}$ and, thereafter, gradually decreased at a diminishing rate up to a dosage $D = 0.150 \text{ ml} \cdot \text{l}^{-1}$. At higher dosages residual turbidity remained almost unchanged. The lowest residual turbidity, $\text{Tu}_{60}\text{F} = 0.30 \text{ NTU}$, was obtained at a dosage $D = 0.150 \text{ ml} \cdot \text{l}^{-1}$. Therefore, this dosage is considered to be the optimum dosage for destabilisation of turbidity particles. The COD_{Mn} value decreased more rapidly up to breakpoint at a dosage $D = 0.100 \text{ ml} \cdot \text{l}^{-1}$ and, thereafter, decreased at a much lower rate. The lowest residual turbidity, $\text{COD}_{\text{Mn}60} = 2.85 \text{ mg O}_2 \cdot \text{l}^{-1}$, was obtained at the maximum dosage applied, $D = 0.175 \text{ ml} \cdot \text{l}^{-1}$. The reaction pH value dropped gradually with dosage from $\text{pH} = 7.15$ to 6.35 at the maximum dosage.

Based on the evaluation of the results obtained with respect to all three pollution determinants, a dosage $D = 0.150 \text{ ml} \cdot \text{l}^{-1}$ is considered to be the operational dosage; the reaction $\text{pH} = 6.5$. Wholesome quality water was not produced due to higher COD_{Mn} value.

Pure CPE

The following CPE of synthetic and natural origin produced by different manufacturers were tested:

- (a) Synthetic: polyDADMAC:
 - L-100: concentration about 20%,
 - M-20: concentration about 20%,
 Polyamine
 - M-500: concentration about 50%,
 - Anikem 8100: concentration about 50%.
- (b) Natural: Wattle tannin based:
 - Belfloc - a blend of Floccotan and polyDADMAC, their assumed ratio is 8:2. Although a blended product, Belfloc is included among the pure CPE because it is a blend of pure organic polymers.

TABLE 3 Comparison of treated water quality attainable by the operational dosages of the different coagulants tested at Saulspoor Waterworks ($Tu^{RW} = 55-75$ NTU, $Me^{RW} = 0.81$ mg $Fe \cdot l^{-1}$, $COD_{MnRW} = 5.9-6.40$ mg $O_2 \cdot l^{-1}$, $pH^{RW} = 7.43-7.94$, $t^{RW} = 14.7$ to 16 °C)										
Coagulant	The best attainable treatability of water with respect to individual determinants by optimum dosages D_o			Treatability of water with respect to all determinants monitored attainable by applicable coagulant dosage D_A and dosage cost indication						
	Me [mg l^{-1}]	COD_{Mn} [mg $O_2 \cdot l^{-1}$]	Tu [NTU]	D_A [mg l^{-1}]	Me [mg l^{-1}]	COD_{Mn} [mg $O_2 \cdot l^{-1}$]	Tu [NTU]	pH [-]	ϕCOD_{Mn} [-]	Dosage cost factor
Hydrolysing coagulants										
$FeCl_3$	0.01	1.19	0.12	75	0.01	1.99	0.25	5.92	0.66	9 855
$Al_2(SO_4)_3$	0.15	2.08	0.12	138	0.15	2.33	0.18	6.07	0.61	12 378
PACI [ml l^{-1}]										
M-30	0.14	2.55	0.15	0.165	0.15	2.64	0.15	6.51	0.55	17 020
K-288	-	2.85	0.30	0.150	0.25	3.02	0.30	6.52	0.50	-
Pure CPE										
L-100	N/A	4.96	1.15	0.002	N/A	4.96	1.90	7.78	0.21	1 163
M-20	N/A	4.64	0.29	0.006	N/A	4.72	0.32	7.62	0.24	3 526
M-500	N/A	4.37	0.77	0.004	N/A	4.46	1.30	7.62	0.30	3 068
ANIKEM 8100	N/A	4.80	1.05	0.004	N/A	5.08	1.60	7.88	0.21	6905
BELFLOC	N/A	5.52	0.26	0.001	N/A	5.52	1.20	7.83	0.12	-
				0.006	N/A	6.72	0.26	7.69	-0.08	-
Blended CPE										
M-101	0	3.84	0.37	0.012	0.00	4.16	0.52	7.55	0.35	5 925
M-182	0	2.42	0.26	0.010	0.00	2.62	0.30	6.14	0.58	2 310
DP-160	0.12	3.68	0.54	0.005	0.12	4.48	1.80	7.44	0.26	2 357
				0.030	0.35	3.68	0.54	7.24	0.39	14 145
ANIKEM 4141	0.22	3.52	0.48	0.005	0.22	4.69	1.95	7.43	0.22	7 085
				0.030	0.38	3.52	0.48	7.19	0.42	42 506

The treatability of water attainable with CPE was tested over a wide range of dosages. The dosages are expressed in $ml \cdot l^{-1}$ of the commercially supplied stock CPE solution. The treatability of water was evaluated only by two pollution determinants Tu_{60} and COD_{Mn60} because evaluation by residual Me is not applicable with pure organic polymers.

Treatability of the water attainable with CPE is shown in Figs. 5 to 9. These Figures illustrate the dependence of changes of the pollution determinants (Tu and COD_{Mn}) on dosage. The treated water quality obtained by the operational dosage of the individual reagents is shown in Table 3.

Synthetic CPE

PolyDADMAC

L-100

Figure 5 shows that turbidity dropped rapidly up to a dosage $D = 0.002$ $ml \cdot l^{-1}$ and, thereafter, it slowed. The lowest residual

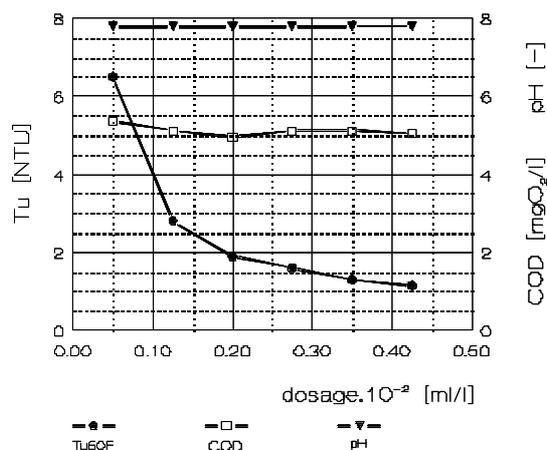


Figure 5
Treatment process efficiency attainable with PACI. Product L-100.

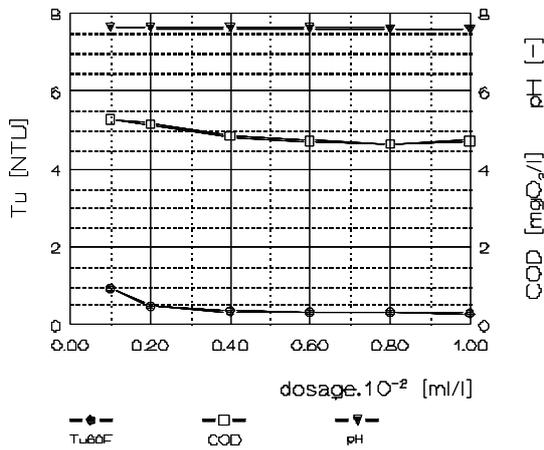


Figure 6

Treatment process efficiency attainable with CPE. Product M-20.

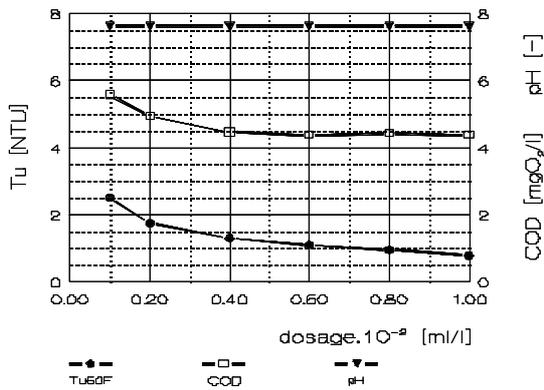


Figure 7

Treatment process efficiency attainable with CPE. Product M-500.

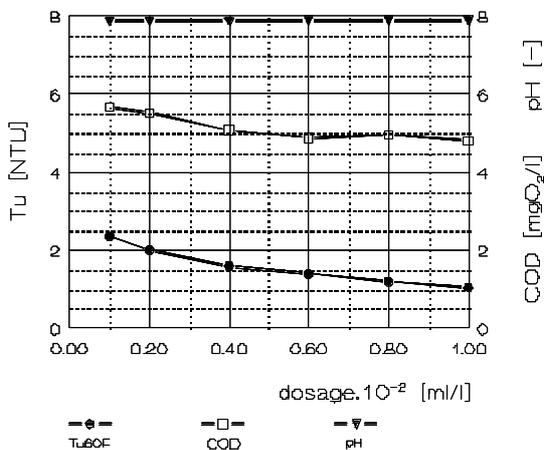


Figure 8

Treatment process efficiency attainable with CPE. Product ANIKEM 8100.

turbidity, $Tu_{60F} = 1.15$ NTU, was obtained at the maximum dosage applied, $D = 0.00425 \text{ ml}\cdot\text{t}^{-1}$. This dosage can be considered to be the optimum dosage for aggregation of turbidity particles. The COD_{Mn} value also decreased very slowly up to breakpoint at a dosage $D = 0.002 \text{ ml}\cdot\text{t}^{-1}$ and, thereafter, remained almost unchanged around $COD_{Mn60} = 5.10 \text{ mg O}_2\cdot\text{t}^{-1}$. The reaction pH value remained stable around 7.93 over the full range of dosages applied.

An acceptable quality treated water could not be produced with any dosage applied.

M-20

Figure 6 shows that turbidity drops rapidly up to a dosage $D = 0.002 \text{ ml}\cdot\text{t}^{-1}$. Thereafter, it gradually diminished and from a dosage $D = 0.004 \text{ ml}\cdot\text{t}^{-1}$ residual turbidity remained almost unchanged. The lowest residual turbidity, $Tu_{60F} = 0.29$ NTU, was obtained at the maximum dosage applied, $D = 0.010 \text{ ml}\cdot\text{t}^{-1}$. This dosage can be considered to be the optimum dosage for aggregation of turbidity particles. The COD_{Mn} value decreased very slowly up to breakpoint at a dosage $D = 0.004 \text{ ml}\cdot\text{t}^{-1}$ and, thereafter, remained almost unchanged around $COD_{Mn60} = 4.70 \text{ mg O}_2\cdot\text{t}^{-1}$. The reaction pH value dropped with dosage only marginally from $\text{pH} = 7.65$ to 7.60 at the maximum dosage.

An acceptable quality treated water could not be produced with any dosage applied.

Polyamine CPE

M-500

Figure 7 shows that turbidity dropped rapidly up to a dosage $D = 0.004 \text{ ml}\cdot\text{t}^{-1}$ and thereafter it gradually decreased at a lower rate. The lowest residual turbidity, $Tu_{60F} = 0.77$ NTU, was obtained at the maximum dosage applied, $D = 0.010 \text{ ml}\cdot\text{t}^{-1}$. The COD_{Mn} value decreased very slowly up to a dosage $D = 0.004 \text{ ml}\cdot\text{t}^{-1}$ and, thereafter, remained virtually unchanged around $COD_{Mn60} = 4.40 \text{ mg O}_2\cdot\text{t}^{-1}$. The reaction pH value remained stable around 7.62 over the full range of dosages applied.

An acceptable quality treated water could not be produced with any dosage applied.

Anikem 8100

Figure 8 shows that turbidity dropped over the full range of dosages applied at a slow, almost constant rate. The lowest residual turbidity, $Tu_{60F} = 1.05$ NTU, was obtained at the highest dosage applied, $D = 0.010 \text{ ml}\cdot\text{t}^{-1}$. The COD_{Mn} value gradually decreased up to a dosage $D = 0.004 \text{ ml}\cdot\text{t}^{-1}$ and, thereafter, decreased very slowly. The lowest residual $COD_{Mn60} = 4.80 \text{ mg O}_2\cdot\text{t}^{-1}$ was obtained at the highest dosage applied, $D = 0.010 \text{ ml}\cdot\text{t}^{-1}$. The reaction pH value remains stable around 7.87 over the full range of dosages applied.

An acceptable quality treated water could not be produced with any dosage applied.

Natural CPE

Belfloc

Figure 9 shows that turbidity dropped rapidly up to breakpoint at a dosage $D = 0.030 \text{ ml}\cdot\text{t}^{-1}$ and, thereafter, it decreased very slowly. The lowest residual turbidity, $Tu_{60F} = 0.26$ NTU, was obtained at a dosage $D = 0.060 \text{ mg}\cdot\text{t}^{-1}$. Therefore, this dosage is considered to be the optimum dosage for aggregation of turbidity particles. Sufficient aggregation efficiency of turbidity particles was achieved at a dosage $D = 0.050 \text{ ml}\cdot\text{t}^{-1}$. In contrast to all other CPE tested, COD_{Mn} value gradually increased over the full range of dosages applied. The lowest residual $COD_{Mn60} = 5.52 \text{ mg O}_2\cdot\text{t}^{-1}$, was

obtained at the lowest dosage applied, $D = 0.010 \text{ mL}\cdot\text{L}^{-1}$. The highest $\text{COD}_{\text{Mn60}} = 6.72 \text{ mg O}_2\cdot\text{L}^{-1}$ was obtained at the highest dosage applied, $D = 0.060 \text{ mL}\cdot\text{L}^{-1}$, representing an increase $\text{COD}_{\text{Mn}} = 0.48 \text{ mg O}_2\cdot\text{L}^{-1}$ in comparison to that of the raw water. The COD_{Mn60} value of the treated water balanced that of the raw water, $\text{COD}_{\text{Mn}}^{\text{RW}} = 6.24 \text{ mg O}_2\cdot\text{L}^{-1}$ at a dosage $D = 0.045 \text{ mL}\cdot\text{L}^{-1}$. The reaction pH value dropped with dosage marginally only from $\text{pH} = 7.83$ to 7.69 at the maximum dosage applied.

An acceptable quality treated water could not be produced with any dosage applied. A typical coagulation curve for COD_{Mn} value was not obtained. Therefore, there is no dosage that can be considered to be the operational dosage.

Blended CPE

Treatability of the water attainable with the blended CPE is shown in Figs. 10 to 13. These Figures illustrate the dependence of changes of the pollution determinants on dosage. The treated water quality obtained by the operational dosage of the individual reagents is shown in Table 3.

The following CPE were tested:

(a) Fe-based CPE

- M-101: a blend of FeCl_3 and polyamine, their assumed ratio is 1:1,
- M-182: a blend of FeCl_3 and polyamine, their assumed ratio is 9:1,

(b) Al-based CPE

- DP-160: a blend of PACl, polyamine and polyDADMAC, their assumed ratio is 6:2:2,
- Anikem 4141: a blend of PACl and polyamine, their assumed ratio is 1:1.

Fe-based CPE

M-101

Figure 10 shows that Fe is completely removed from the water over the full range of dosages applied. Turbidity dropped rapidly up to breakpoint at a dosage $D = 0.004 \text{ mL}\cdot\text{L}^{-1}$ and, thereafter, it decreased slowly up to the maximum dosage applied. The lowest residual turbidity, $\text{Tu}_{60\text{F}} = 0.37 \text{ NTU}$, was obtained at the maximum dosage applied $D = 0.024 \text{ mL}\cdot\text{L}^{-1}$. The COD_{Mn} value also dropped fairly rapidly to breakpoint at a dosage $D = 0.012 \text{ mL}\cdot\text{L}^{-1}$ and, thereafter, it decreased very slowly up to the maximum dosage. The lowest residual COD_{Mn} value, ($\text{COD}_{\text{Mn60}} = 3.84 \text{ mg O}_2\cdot\text{L}^{-1}$), was obtained at the maximum dosage $D = 0.024 \text{ mL}\cdot\text{L}^{-1}$. The reaction pH value dropped with dosage marginally only from $\text{pH} = 7.83$ to 7.35 at the maximum dosage.

An acceptable quality treated water could not be produced with any dosage applied.

M-182

Figure 11 shows that Fe is completely removed from the water over the full range of dosages applied. Turbidity gradually dropped over the full range of dosages applied. The lowest residual turbidity, $\text{Tu}_{60\text{F}} = 0.26 \text{ NTU}$, was obtained at the maximum dosage applied $D = 0.148 \text{ mL}\cdot\text{L}^{-1}$. This dosage can be considered to be the optimum dosage for aggregation of turbidity particles. Sufficient aggregation efficiency of turbidity particles was achieved at a dosage $D = 0.10 \text{ mL}\cdot\text{L}^{-1}$. The COD_{Mn} value also dropped fairly rapidly to breakpoint at a dosage $D = 0.075 \text{ mL}\cdot\text{L}^{-1}$ and, thereafter, it decreased very slowly. The lowest residual COD_{Mn} value, $\text{COD}_{\text{Mn60}} = 2.42 \text{ mg O}_2\cdot\text{L}^{-1}$, was obtained at the maximum dosage $D = 0.148 \text{ mL}\cdot\text{L}^{-1}$.

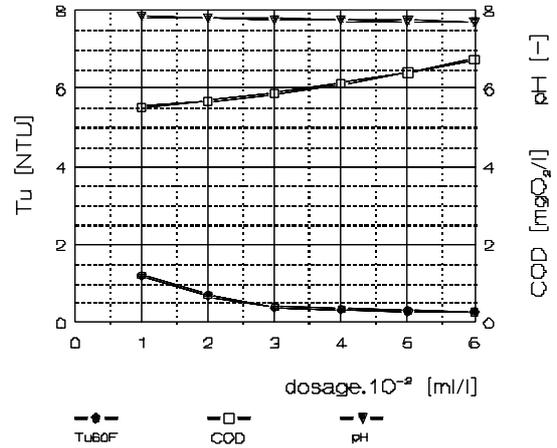


Figure 9
Treatment process efficiency attainable with CPE.
Product BELFLOC.

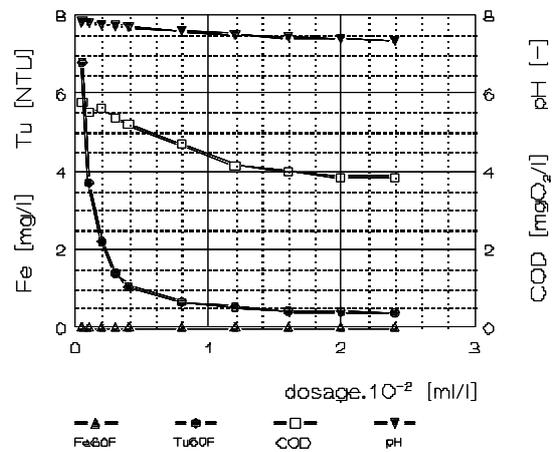


Figure 10
Treatment process efficiency attainable with CPE. Product M-101.

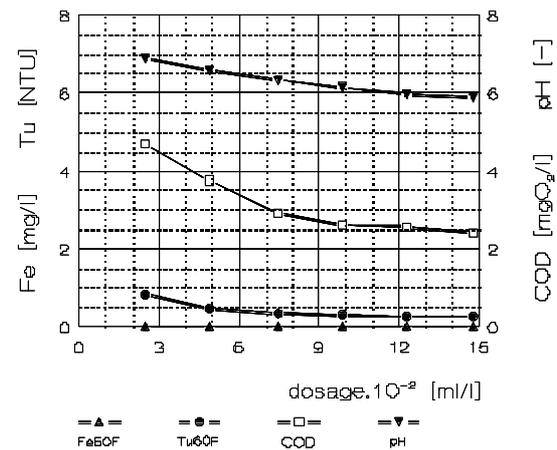


Figure 11
Treatment process efficiency attainable with CPE. Product M-182.

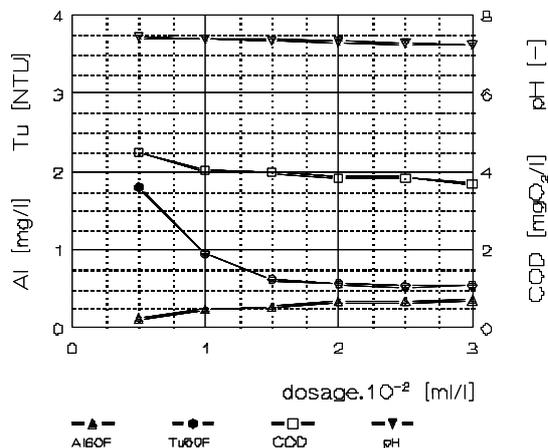


Figure 12
Treatment process efficiency attainable with CPE.
Product DP-160.

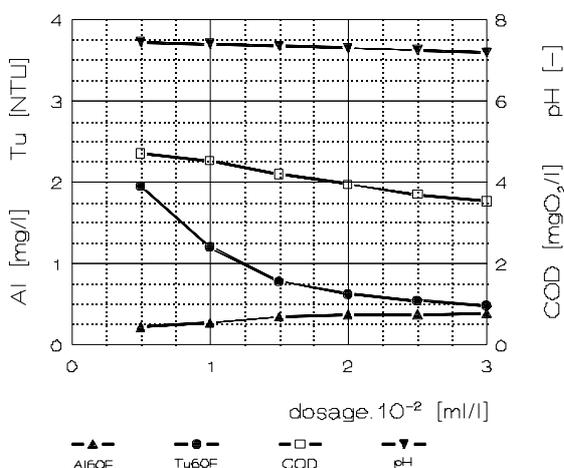


Figure 13
Treatment process efficiency attainable with CPE.
Product ANIKEM 4141.

The reaction pH value dropped gradually with dosage from pH = 6.87 to 5.89 at the maximum dosage.

An acceptable quality treated water could not be produced with any dosage applied.

Al-based CPE

DP-160

Figure 12 shows that the residual Al content slowly increases at a gradually reducing rate from $Me_{60}F = 0.22 \text{ mg Al}\cdot\text{t}^{-1}$ at the minimum dosage to $Me_{60}F = 0.38 \text{ mg Al}\cdot\text{t}^{-1}$ at the maximum dosage. Turbidity dropped fairly rapidly up to breakpoint at a dosage $D = 0.015 \text{ ml}\cdot\text{t}^{-1}$ and, thereafter, it decreases very slowly up to a dosage $D = 0.025 \text{ ml}\cdot\text{t}^{-1}$. From this dosage onward residual turbidity remained unchanged. The lowest residual turbidity, $Tu_{60}F = 0.53 \text{ NTU}$, was obtained at a dosage $D = 0.025 \text{ ml}\cdot\text{t}^{-1}$. The COD_{Mn} value gradually decreased over the full range of dosages applied. The lowest $COD_{Mn60} = 3.68 \text{ mg O}_2\cdot\text{t}^{-1}$ was measured at the maximum dosage, $D = 0.030 \text{ ml}\cdot\text{t}^{-1}$. The reaction pH value dropped with dosage only marginally from pH = 7.44 to 7.24 at the maximum dosage.

An acceptable quality of the treated water could not be produced with any dosage applied. A typical coagulation curve for residual

Al was not obtained. Therefore, there is no dosage that can be considered to be the operational dosage.

Anikem 4141

Figure 13 shows that the residual Al content slowly increases at a reducing rate from $Me_{60}F = 0.22 \text{ mg Al}\cdot\text{t}^{-1}$ at the minimum dosage to $Me_{60}F = 0.38 \text{ mg Al}\cdot\text{t}^{-1}$ at the maximum dosage. Turbidity dropped fairly rapidly up to breakpoint at a dosage $D = 0.015 \text{ ml}\cdot\text{t}^{-1}$ and, thereafter, its drop gradually decreased up to the maximum dosage $D = 0.030 \text{ ml}\cdot\text{t}^{-1}$. The lowest residual turbidity, $Tu_{60}F = 0.48 \text{ NTU}$, was obtained at the maximum dosage. The COD_{Mn} value gradually decreased over the full range of dosages applied. The lowest $COD_{Mn60} = 3.52 \text{ mg O}_2\cdot\text{t}^{-1}$ was measured at the maximum dosage, $D = 0.030 \text{ ml}\cdot\text{t}^{-1}$. The reaction pH value dropped with dosage only marginally from pH = 7.43 to 7.19 at the maximum dosage.

An acceptable quality treated water could not be produced with any dosage applied. A typical coagulation curve for residual Al was not obtained. Therefore, there is no dosage that can be considered to be the operational dosage.

Influence of reaction pH on the removal of organic matter by CPE

It is evident from the foregoing that a considerable difference in the treatment process efficiency between CPE and hydrolysing reagent exists. It seems that this difference could be connected to reaction pH value. It is evident from Figs. 1 to 4 that the reaction pH dropped considerably when treatment is by hydrolysing reagents and that the treatment process efficiency with respect to the removal of organic matter gradually increased with decreasing pH value. On the contrary, Figs. 5 to 9 show the reaction pH value of water treated by CPE remained almost unchanged in comparison to that of the raw water and the treatment process efficiency achieved with respect to the removal of organic matter was found to be insignificant. Therefore, the influence of the reaction pH value on the efficiency of removing organic pollution (COD_{Mn} value) by CPE was also investigated.

The raw water was pre-treated by different dosages of H_2SO_4 prior to the addition of CPE. The tests were carried out with L-100 at a constant dosage $D = 0.002 \text{ ml}\cdot\text{t}^{-1}$ and Belfloc at a constant dosage $D = 0.030 \text{ ml}\cdot\text{t}^{-1}$. The results obtained are plotted in Figs. 14 and 15. Pre-acidification of the water improved removal of turbidity by both CPE. In the case of polyDADMAC L-100, residual turbidity dropped from $Me_{60}F = 1.80$ to 1.50 NTU as a result of lowering the reaction pH value from 7.73 to 5.76. In the case of Belfloc, lowering of the reaction pH value from 7.45 to 5.98 resulted in reducing the $Me_{60}F$ value from 0.40 to 0.31 NTU. Regarding removal of organic matter, pre-acidification of the water did not change COD_{Mn60} value at all in the case of polyDADMAC L-100 (Fig. 14). In the case of Belfloc, preacidification of the water caused the COD_{Mn60} value to drop slightly from $6.32 \text{ mg O}_2\cdot\text{t}^{-1}$ to approximately $5.50 \text{ mg O}_2\cdot\text{t}^{-1}$.

Secondary organic pollution of water caused by CPE

The existence of secondary organic pollution is evident from the comparison of DOC, COD_{Mn} and TOH_p values measured in the raw water and the treated water.

The potential of the CPE to cause secondary organic pollution was established at Saulspoot Waterworks during 1983, when Floccotan was used as the coagulant. Its extent is evident from the

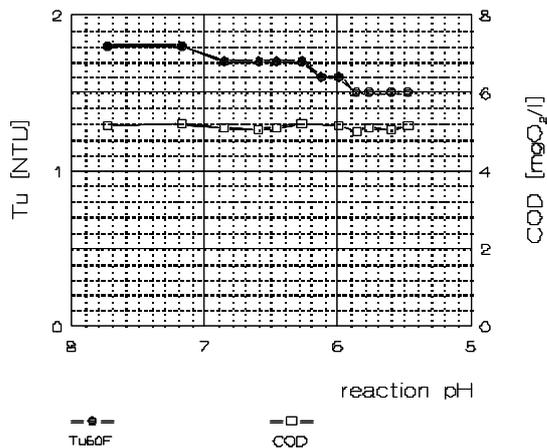


Figure 14
Influence of reaction pH.
Product L-100. $D = 0.0002 \text{ ml/l}$

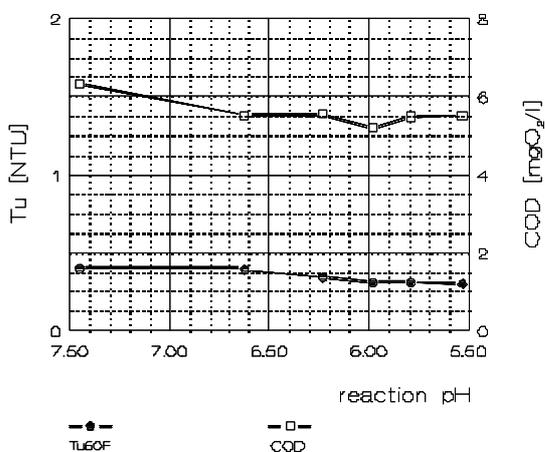


Figure 15
Influence of reaction pH.
Product BELFLOC. $D = 0.03 \text{ ml/l}$

results in Table 2. Although DOC value was reduced slightly by the treatment process, the TOH_p value increased by almost 40% in comparison to that of the raw water. This indicates that while the overall organic pollution was reduced slightly, an undesirable residue of CPE, producing considerable additional concentration of TOH precursors, remained in the treated water.

Another example of the existence of secondary pollution produced by CPE is evident from the tests with Belfloc, described in the foregoing and shown in Fig 9. These tests showed that when water was treated to produce the lowest residual turbidity, CPE effectively polluted the treated water to the extent that the COD_{Mn} value of the treated water was higher than that of the raw water.

Discussion of the results obtained

The dependence of changes of the pollution determinants on dosage of the coagulants tested is shown in Figs. 1 to 13. The quality to which the raw water was treatable by their respective optimum and applicable dosages are presented in Table 3. It should be pointed out that the applicable dosage D_A corresponds to the operational dosage only in case of the hydrolysing coagulants. In case of all the CPE, pure or blended, the applicable dosage D_A

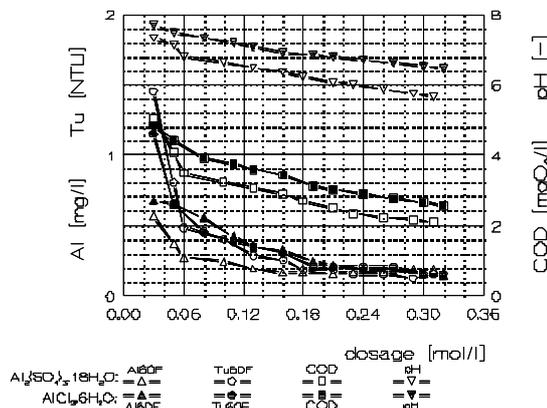


Figure 16
Comparison of treatment efficiency of $\text{Al}_2(\text{SO}_4)_3$ with PACI

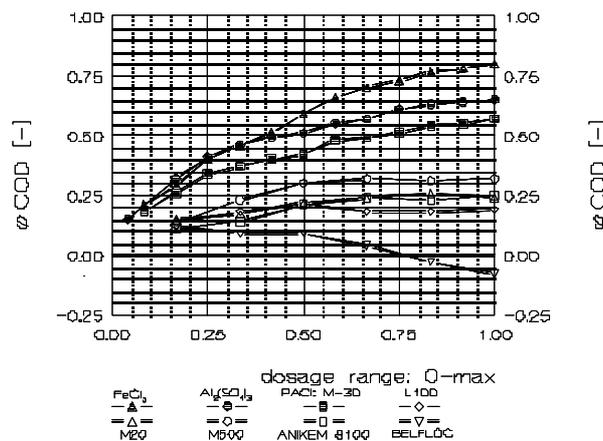


Figure 17
Comparison of sep. efficiencies of organic matter by pure coagulants

corresponds to a dosage that would be applied at the waterworks should the particular coagulant be used, irrespective of its technological suitability.

The effect of pre-acidification of the water on changes in removal of turbidity and organic matter by different CPE is shown in Figs. 14 and 15. Comparison of the treatment process efficiency obtained by the same dosages of aluminium sulphate and PACI (M-30) is shown in Fig. 16. The dependence of separation efficiency of organic matter, $\phi\text{COD}_{\text{Mn}}$, on dosage of all coagulants tested is compared in Figs. 17 to 19. The separation efficiencies attainable by the CPE with that attainable by hydrolysing reagents are compared in Fig. 17. The separation efficiencies attainable by blended Fe-based CPE with that attainable by ferric chloride are compared in Fig. 18 and those attainable by blended Al-based CPE with that by aluminium sulphate and PACI are compared in Fig. 19. It should be noted that dosages indicated in Figs. 17 to 19 represent a span between 0 and maximum dosage applied, which is expressed by unit ratio.

The dependence of the treated water quality on dosage rate of different hydrolysing reagents is shown in Figs. 1 to 4. The water was treatable to within the limits set out for wholesome quality water only with ferric chloride. Aluminium sulphate was found to be less effective. This was expected because aluminium sulphate is not particularly effective for the treatment of high alkalinity and

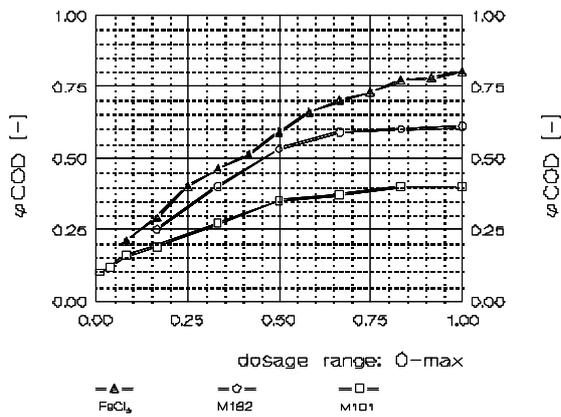


Figure 18

Comparison of sep. efficiencies of organic matter by Fe-based coagulants

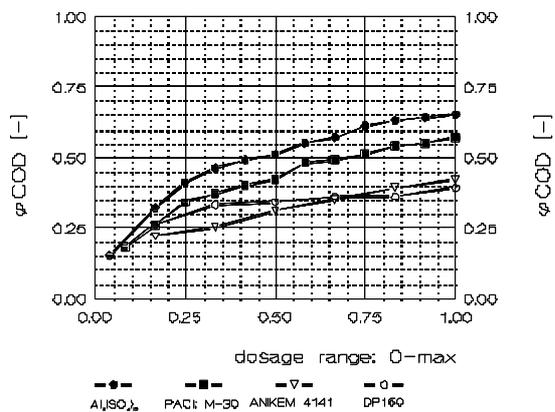


Figure 18

Comparison of sep. efficiencies of organic matter by Al-based coagulants

high ionic strength waters as is the Saulspoor Dam water. On the other hand, aluminium sulphate was found to be more effective than any of the PACl tested. A comparison of the treated water quality obtained with PACl showed that M-30 is more efficient than K-288. This is probably a result of different degrees to which $AlCl_3$ in both PACl were pre-polymerised. Ferric chloride is considered to be the most suitable hydrolysing coagulant for treatment of the Saulspoor Dam water.

A comparison of Tu_{60} , Me_{60} and COD_{Mn60} values obtained by PACl with those obtained by aluminium sulphate (Figs. 2 to 4 and 16) shows PACl to be less efficient with respect to the removal of organic matter and residual Al, but on par with respect to the removal of turbidity. Hence, the treatment process efficiency achieved by PACl was found to be considerably lower than that by aluminium sulphate. The reaction pH value determines the form of the destabilisationally effective polymers that originate during hydrolysis, the hydroxopolymer, and the space arrangement of the chains of the organic matter. The optimum reaction pH at which the highest removal of organic impurities is achieved, is usually between pH = 4 to 6.

It should be emphasised that residual Me is solubility dependent which, in turn, is reaction pH- dependent. In the case of aluminium sulphate, its minimum solubility is obtained at a pH of 4.5 and with increasing pH value its solubility increases. PACl is characterised by a lower acidity equivalent than that of aluminium sulphate.

Therefore, a much higher dosage of PACl is required to produce the same reaction pH as that produced by aluminium sulphate, as is evident from Fig. 16.

It is evident from Figs. 1 to 4 that the COD_{Mn} value slowly decreases with dosage and its lowest value is obtained in the range of higher dosages, where pH value is lower and the macromolecule chains are unravelled, thus making further functional groups accessible to the particles of destabilisation reagent. For these reasons, the lowest COD_{Mn} value is obtained at a higher dosage than that at which the lowest Me content is achieved.

The dependence of the treated water quality on dosage rate of CPE is shown in Figs. 5-9. A comparison of the results in Figs. 5 and 6 shows that neither of the polyDADMAC reagents (M-20, L-100) was capable of any meaningful removal of organic matter from the water. However, M-20 was evidently capable of treating the water to sparkling clarity, while L-100 was not. With respect to the removal of organic pollution, M-20 was again marginally more efficient than L-100. The only explanation for the differences in the process efficiency between these two polyDADMAC reagents having the same solids content is that the polyDADMAC used in L-100 is of different formulation than that used in M-20.

A comparison of the results in Figs. 7 and 8 shows that neither of the polyamine reagents (M-500, Anikem 8100) was capable of any meaningful removal of organic matter from the water, although M-500 seems to be marginally more efficient than Anikem 8100. Further, it shows that neither of these CPE was capable of treating the water to sparkling clarity, although again M-500 seems to be marginally more efficient. The only explanation for these small differences in the treatment process efficiencies is that the polyamine used in Anikem 8100 is of a different formulation than that used in M-500. Furthermore, Table 3 shows that the M-500 reagent dosage cost is considerably smaller than that of Anikem 8100.

The quantities of different types of particles of organic impurities removed by the dosage-cost cheapest hydrolysing reagent ($FeCl_3$) and CPE (L-100) (similar situation applies to all other CPE), are compared in Table 4. The particles of impurities aggregated during the treatment process are those of dissolved organic impurities that are capable of specific adsorption onto the surface of the formed suspension at the reaction pH of the system. In comparison, the quantity of organic impurities aggregated by the treatment with $FeCl_3$ was more than 10 times larger.

The dependence of the treated water quality on Belfloc dosage is shown in Fig. 9. As can be seen from this figure, considerable secondary organic pollution of the water occurred. This is evident by the COD_{Mn60} value rapidly increasing with increasing Belfloc dosage. The extent of this secondary organic pollution was such that it exceeded the quantity of organic impurities actually removed. A situation arose when the quantity of organic matter removed and that originating from treatment by the Belfloc treatment were in balance at a dosage $D = 0.045 \text{ mL}^{-1}$, corresponding to $\phi COD_{Mn} = 0.0$. At higher Belfloc dosages the treated water had greater organic pollution (higher COD_{Mn} value) than that of the raw water. Furthermore, a typical coagulation curve for COD_{Mn} value was not obtained. Due to this, Belfloc has no dosage that can be considered to be the operational dosage and this makes Belfloc a totally undesirable reagent for the treatment of drinking water.

The dependence of the treated water quality on dosage of blended CPE is shown in Figs. 10 to 13. The blended Fe-based CPE were found to be less efficient with respect to the removal of organic impurities than ferric chloride, but considerably more efficient than the blended PACl-based CPE, which were found to be rather inefficient. In the case of Fe-based CPE, Fe was removed completely. In contrast, the residual Al remaining in the water

Type of particles	Reading	FeCl ₃	L-100
Total quantity of particles in the raw water	COD _{MnRW}	5.93	6.24
Quantity of non-separable particles in the raw water	COD _{MnRW} ^F	5.38	5.36
Quantity of particles in a particulate, separable form in the raw water	ΔCOD _{MnRW-P}	0.55	0.88
Total quantity of particles in the raw water	COD _{MnRW}	5.93	6.24
Total quantity of particles remaining in the treated water	COD _{Mn60}	1.19	4.96
Total quantity of particles removed by treatment	ΔCOD _{MnTW-T}	4.74	1.28
Total quantity of particles removed by treatment	ΔCOD _{MnTW-T}	4.74	1.28
Total quantity of particles in particulate, separable form	ΔCOD _{MnRW-P}	0.55	0.88
Total quantity of non-separable particles removed by treatment	ΔCOD _{MnTW-N}	4.19	0.40

treated by blended PACI-based CPE was higher than that obtained with treatment by aluminium sulphate. Furthermore, residual Al was found to increase gradually with dosage over the full range of dosages applied, well above the preset limiting concentration, $c = 0.15 \text{ mg Al} \cdot \text{t}^{-1}$. This is the result of higher reaction pH in comparison to that of aluminium sulphate. Furthermore, a comparison of the results obtained also shows that it is the Me component that is effective and that the treatment efficiency increases with the Me content in the CPE. The organic polymer component in the CPE is destabilisationally ineffective.

As can be seen from the results in Figs. 14 and 15, different reaction pH values did not affect the overall treatment process efficiency attainable by CPE of synthetic (polyDADMAC) and natural (Belfloc) origin in any meaningful way. Hence, the effect of reaction pH on the removal of organic matter by treatment with CPE is rather low. Consequently, the differences in separation efficiencies between hydrolysing coagulants and CPE result from their different mechanisms, enabling particle aggregation. The separation of impurities by hydrolysing coagulants includes those mechanisms for which the prerequisite for aggregation is the preceding destabilisation of the impurities, the efficiency of which is determined, to a great extent, by the type of the hydroxopolymer being formed. The predominating type of the hydroxopolymer changes with pH value and is most destabilisationally effective at $\text{pH} = 4$ to 6 . The conditions for destabilisation are determined by the chemical composition of impurities and, in particular, by the structure of organic matter, which is also pH-dependent. These aspects determine the selection of a suitable hydrolysing coagulant, width of destabilisation optimum, operational dosage and reaction pH value. In contrast, CPE probably functions as destabilisation reagents only in the case of solid mineral particles. They do not cause destabilisation of organic impurities - their separation is a result of aggregation of impurities caused mainly by the mechanism of interparticle bridging and partly by the mechanism of particle enmeshment.

Separation efficiencies with respect to organic matter (COD_{Mn} value) achieved by pure coagulants, both hydrolysing and CPE, are compared in Fig. 17. The separation efficiencies with respect to the same determinant achieved by the blended Fe-based CPE and ferric chloride are compared in Fig. 18 and by the blended Al-based CPE are compared with aluminium sulphate and PACI in Fig. 19. The lowest attainable residual values of the three determinants together with their residual values attained by the operationally applicable dosages of coagulants tested are compared in Table 3.

Mutual comparison of the results in Figs. 1 to 9 and 17 shows that hydrolysing coagulants, and in particular ferric chloride, responded very effectively to the removal of all three pollution determinants and all were well below the preset limiting values, i.e. $\text{COD}_{\text{Mn}} \leq 2.0 \text{ mg O}_2 \cdot \text{t}^{-1}$, $\text{Me} \leq 0.15 \text{ mg} \cdot \text{t}^{-1}$ and $\text{Tu} \leq 0.15 \text{ NTU}$. The highest separation efficiency with respect to the removal of organic impurities was produced by ferric chloride $\phi\text{COD}_{\text{Mn}} = 80\%$ ($\text{COD}_{\text{Mn60}} = 1.19 \text{ mg O}_2 \cdot \text{t}^{-1}$). The separation efficiency attainable by aluminium sulphate was lower, $\phi\text{COD}_{\text{Mn}} = 65\%$ ($\text{COD}_{\text{Mn60}} = 2.08 \text{ mg O}_2 \cdot \text{t}^{-1}$) due to the chemical composition of the water, but was on par with the desired COD_{Mn} value. The separation efficiency attainable by PACI was very low and exceeded the desired COD_{Mn} value, $\phi\text{COD}_{\text{Mn}} = 57\%$ ($\text{COD}_{\text{Mn60}} = 2.55 \text{ mg O}_2 \cdot \text{t}^{-1}$). In comparison to hydrolysing reagents, the separation efficiencies of polyDADMAC and polyamine CPE were found to be totally insignificant, $\phi\text{COD}_{\text{Mn}} = 22$ to 32% ($\text{COD}_{\text{Mn60}} = 4.96$ to $4.37 \text{ mg O}_2 \cdot \text{t}^{-1}$). Neither of the CPE was capable of treating the water to within the above pollution determinant limits. In the case of wattle tannin extract based natural CPE, its separation efficiency decreases continuously, proportionately to dosage over the full range of dosages applied, $\phi\text{COD}_{\text{Mn}} = -8$ to 14% ($\text{COD}_{\text{Mn60}} = 6.72$ to $5.52 \text{ mg O}_2 \cdot \text{t}^{-1}$). The negative value means that the secondary pollution caused by this CPE was of such a magnitude that it exceeded the quantity of organic matter removed by the treatment process, making the treated water more polluted than the raw water.

Comparison of the results of the treatability of water attainable by blended Fe-based CPE with that of ferric chloride (Figs. 10, 11 and 18 and Table 3) shows ferric chloride to be considerably more efficient for the removal of organic matter than either of the blended Fe-based CPE, namely M-182 and M-101. The best separation efficiency was obtained with ferric chloride, $\phi\text{COD}_{\text{Mn}} = 80\%$ ($\text{COD}_{\text{Mn60}} = 1.19 \text{ mg O}_2 \cdot \text{t}^{-1}$). The separation efficiency obtained with M-182 (containing about 90% ferric chloride) was $\phi\text{COD}_{\text{Mn}} = 61\%$ ($\text{COD}_{\text{Mn60}} = 2.42 \text{ mg O}_2 \cdot \text{t}^{-1}$). The lowest separation efficiency was obtained with M-101 (containing about 50% ferric chloride) $\phi\text{COD}_{\text{Mn}} = 40\%$ ($\text{COD}_{\text{Mn60}} = 3.84 \text{ mg O}_2 \cdot \text{t}^{-1}$). Further, the separation efficiencies of M-182 or M-101 in removing Me were on par and Tu was below those obtained with ferric chloride. The differences between the separation efficiencies decreases with an increasing content of Fe-salt in the CPE.

Comparison of the results of the treatability of water attainable by blended PACI-based CPE with that by aluminium sulphate and pure PACI (Figs. 12, 13 and 19 and Table 3) shows aluminium sulphate to be considerably more effective overall than PACI and

the blended PACI-based CPE. The best separation efficiency with respect to organic matter was obtained with aluminium sulphate, $\phi\text{COD}_{\text{Mn}} = 65\%$ ($\text{COD}_{\text{Mn60}} = 2.08 \text{ mg O}_2 \cdot \text{L}^{-1}$). The separation efficiency obtained with PACI (M-30) was $\phi\text{COD}_{\text{Mn}} = 57\%$ ($\text{COD}_{\text{Mn60}} = 2.55 \text{ mg O}_2 \cdot \text{L}^{-1}$) only. The lowest separation efficiencies were obtained with blended PACI-based CPE: $\phi\text{COD}_{\text{Mn}} = 39\%$ ($\text{COD}_{\text{Mn60}} = 3.68 \text{ mg O}_2 \cdot \text{L}^{-1}$) with DP-160 (containing about 50% PACI) and $\phi\text{COD}_{\text{Mn}} = 42\%$ ($\text{COD}_{\text{Mn60}} = 3.52 \text{ mg O}_2 \cdot \text{L}^{-1}$) with Anikem 4141 (containing about 60% PACI). The highest separation efficiency with respect to turbidity was obtained with aluminium sulphate and the lowest one with blended PACI-based CPE. The best separation efficiency with respect to residual Al was obtained with aluminium sulphate and PACI. In contrast to aluminium sulphate and PACI, the separation efficiency of the blended PACI-based CPE was found to decrease with increasing dosage rate. Evidently, blended PACI-based CPE did not create conditions for effective removal of the respective pollutants.

Data in Table 3 show that some CPE are cheaper to apply than destabilisation reagents when dosage cost factors alone are compared. When the quality of treated water is also considered, evidently, there is no justification whatsoever for using any CPE at all.

Furthermore, it follows from Table 3 that ferric chloride was not only the most efficient but also, from a dosage-cost point of view, the cheapest hydrolysing reagent. PACI was found to be both less efficient and, from a dosage-cost point view, also considerably more expensive than aluminium sulphate. Therefore, the use of PACI is neither technologically nor economically justifiable.

It follows from the foregoing that CPE are considerably less efficient coagulants overall in comparison to hydrolysing reagents and that CPE should not be used as coagulant for treatment of waters with significant organic pollution. Therefore, CPE is not an equivalent substitute for hydrolysing coagulants. Based on experience, certain CPE may be found to be of some benefit, but only for treatment of waters with insignificant organic pollution.

Figures 14 and 15 show that adjustment of reaction pH value does not improve quality to which water is treatable by CPE. Consequently, much higher separation efficiencies achieved by destabilisation reagents than those attainable by CPE result from different mechanisms enabling particle aggregation.

The differences in separation efficiencies between hydrolysing reagents and CPE have their origin in the mechanisms by which these reagents aggregate the particles of impurities.

Separable aggregates are formed by two groups of mechanisms:

- The first group is represented by the mechanisms for which the prerequisite of aggregation is destabilisation of particles, i.e. the energy barrier between colliding particles is either totally removed or suppressed to such an extent that it can be forcibly overcome by the high kinetic energy of the colliding particles.
- The second group is represented by the mechanisms for which direct reactions, physical or chemical, take place between the particles of impurities and the particles of coagulant as well as between the particles of impurities and the aggregates already formed.

The first group represents the mechanisms by which hydrolysing reagents function and the second group those by which the CPE function.

The impurities of hydrophobic character are mainly stabilised by a surface, usually negative charge (electric double layer). The impurities of hydrophilic character are stabilised by hydration layer and their negative charge is caused by ionisation of carboxyl and phenolic functional groups ($-\text{COOH}$ and $-\text{OH}$). The stabilisation

energy of the particles is concentrated only in certain places, the active centres, which are located on the surface of hydrophobic particles, such as corners and edges, and in the functional groups of hydrophilic particles (organic molecules).

The chemical structure of the particles determines distribution of the active centres on their surface and for a given impurity this is unchangeable. Their physical configuration determines accessibility of the active centres to the particles of hydrolysing reagent. The products of hydrolysis, the hydroxocomplexes, bind themselves onto the particles of impurities just and only in these active centres and neutralise their charge with the charge they carry, thus destabilising them.

The particles of impurities of different composition have their active centres accessible at different pH values. Their configuration changes depending on the reaction conditions (dosage and pH). At low pH values open configuration predominates and at high pH values close configurations prevail. In open configuration, the active centres are more accessible than in the close configuration.

Therefore, particle aggregation proceeds easily when the hydrophilic particles are of an open, chain type, or the macromolecule chains unravel due to the optimised reaction conditions and the functional groups become accessible. In contrast, it proceeds with difficulty when the hydrophilic particles are of a chain-like configuration and the functional groups are closed in the molecule.

For these reasons, treatment of surface waters should almost always take place in an acidic pH range.

Mechanisms of aggregational destabilisation

The individual mechanisms of aggregational destabilisation can be distinguished as follows (Polasek and Mutl, 1995a):

- 1 Destabilisation of the particles of impurities by the suppression of their electric double-layer by a simple electrolyte.
- 2 Destabilisation of the particles of impurities by the specific adsorption of the products of hydrolysis of Al and Fe salts accompanied by charge neutralisation.
- 3 Destabilisation of the particles of impurities by co-ordination reactions between functional groups contained in the particles of impurities and the metal ions of hydroxopolymers, thus changing the magnitude of the charge of the particles of impurities.
- 4 Formation of inter-particle bridges between the particles of impurities on one hand and the particles of the products of hydrolysis of hydrolysing reagent, or by organic flocculants (polyelectrolytes) on the other hand.
- 5 Enmeshment of the particles of impurities in a precipitate.
- 6 Adsorption of the particles of impurities onto the surface of aggregates already formed.

Mechanism 1 is the main mechanism by which the hydrophobic particles are destabilised by reducing their ζ -potential. Mechanism 2 is considered to be most effective for the destabilisation of hydrophobic and mechanism 3 of hydrophilic particles. Hydrolysing reagents destabilise the particles of impurities by means of these mechanisms. In the treatment of natural waters containing mixtures of different impurities, a combination of these basic mechanisms is complemented to a greater or lesser extent by all the other mechanisms mentioned above. In contrast to hydrolysing reagents, mechanism 4 is the basic mechanism by which CPE function, it can be complemented to a greater or lesser extent by mechanisms 5 and 6 only. Due to that, the CPE efficiency for the removal of hydrophilic impurities is almost insignificant and, for these reasons, they are not equivalent substitutes for hydrolysing reagents.

Conclusions

- 1 Some of surface waters in South Africa can be characterised as waters with technologically significant organic pollution. These waters can be treated to a very high quality by a suitable hydrolysing coagulant, but not to any meaningfully good quality by the CPE. None of the CPE was found to be capable of treating water to the same quality as hydrolysing reagents. The CPE were found to be ineffective for the removal of organic pollution and most are also not even capable of treating water to a sparkling clarity. Furthermore, it was found that some of the natural-type CPE are potential sources of objectionable secondary organic pollution.
- 2 Due to the very low overall treatment process efficiency, no CPE was found to be an equivalent substitute for hydrolysing coagulants. Therefore, CPE should be used with great caution after a thorough investigation and only for treatment of water with technologically insignificant organic pollution.
- 3 PACl, the CPE of a synthetic origin and blended Fe-based CPE produce typical coagulation curves. In contrast, no such curves were obtained by CPE of natural origin and blended PACl-based CPE with respect to some of the pollution determinants.
- 4 The mechanisms of particle aggregation by which hydrolysing coagulants function, is considerably more efficient for the removal of organic impurities than the mechanism of inter-particle bridging, by which CPE function. As a result, treatment by CPE is capable of improving only the appearance of water, but not its true quality in any meaningful way.
- 5 While aluminium sulphate and PACl were found to be on par with respect to their efficiencies for the removal of turbidity and Al, PACl was found to be less efficient for the removal of organic matter.
- 6 The lower treatment process efficiency attainable by PACl together with higher coagulant dosage-cost in comparison to aluminium sulphate does not justify replacement of aluminium sulphate with PACl. Such replacement can result in treating water to a considerably poorer quality at increased operating costs in comparison to that attainable by aluminium sulphate.
- 7 The use of blended CPE is not technologically justifiable. When the use of CPE is essential for plant operation, it is more beneficial to use hydrolysing coagulant on its own and to apply a suitable CPE as an aggregation aid, also on its own, to the most suitable point in the process of particle aggregation.
- 8 Since the attainable quality of treated water together with possible secondary pollution are dependent on the type of CPE and its dosage, application of any CPE should ALWAYS be preceded by a positive outcome of a thorough evaluation of all aspects influencing treatment process efficiency and the quality of the treated water. Since CPE usually require a greater energy input into the process of aggregation than aggregation by means of hydrolysing reagents, the design of each individual process unit should be thoroughly appraised with respect to its suitability for optimal application of the CPE.
- 9 The CPE manufacturers and suppliers should not be allowed to hide the quality of their products behind trade names and Health Department Certificates only, thus confusing the proper identification of CPE. They should be compelled to provide, as a rule, a complete technical specification and composition of each CPE supplied under any trade name. Furthermore, they should be compelled to provide simple methods for measuring the content of active components of the CPE (incoming control of product received by the works) and its residue in the treated water.

- 10 The treated water quality results obtained prove beyond any doubt that the residual turbidity criterion alone used for monitoring and evaluation of waterworks performance does not characterise the true quality of the treated water and should be broadened to include determination of other quality determinants such as residual metal component Me of the coagulant used and organic matter characterised by DOC or COD_{Mn} value.

Symbols

COD _{Mn}	- chemical consumption of oxygen required for oxidation of the oxidisable substances by potassium permanganate under boiling conditions - it characterises the content of organic matter in drinking water
COD _{Mn} ^{RW}	- total COD _{Mn} value of raw water
COD _{Mn} ^{RWF}	- COD _{Mn} value of raw water produced by non-separable particles
COD _{Mn60}	- corresponds to total residual content of organic matter remaining in treated water after 60 min sedimentation
D _A	- applicable coagulant dosage
\bar{G}	- square root mean velocity gradient
Me	- metal or metal component of hydrolysing coagulant
Me ^{RW}	- dissolved metal in raw water
Me ₆₀	- total residual metal component of hydrolysing reagent remaining in treated water after 60 min sedimentation
Me ₆₀ ^F	- residual metal component of hydrolysing coagulant in the treated water produced by nonseparable particles in the Me ₆₀ sample
pH ^{RW}	- pH of raw water
TOH _p	- total organohalogens, potential value
TOH _T	- total organohalogens, terminal value
Tu	- turbidity
Tu ^{RW}	- total turbidity of raw water
Tu ^{RWF}	- turbidity of raw water produced by nonseparable particles
Tu ₆₀	- total residual turbidity remaining in treated water after 60 min sedimentation
Tu ₆₀ ^F	- residual turbidity of treated water produced by non-separable particles in the Tu ₆₀ sample
t ^{RW}	- temperature of raw water
φ _{COD}	- separation efficiency of the treatment process with respect to organic pollution.

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