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Optimization of the polyelectrolyte dosage for dewatering sewage sludge suspensions by means of a new centrifugation analyser with an optoelectronic sensor

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Abstract The flocculation of sewage sludge with poly(diallyldimethylammonium chloride) (PDADMAC) as well as cationic, poly[acrylamide-*co*-(*N,N,N*-trimethylammoniummethylacrylate chloride)] (PTAC), and anionic acrylamide copolymers, poly(acrylamide-*co*-acrylate) (PAAM/AA), was investigated by using a new method to evaluate the velocity of centrifugal separation and the packing behaviour of the sediments. By means of a centrifugation analyser with an optoelectronic measuring system the position of the centrate/sediment interface of the conditioned suspensions can be determined as a function of the separation time, which allows the polyelectrolyte dosage to be optimized for various rotational speeds. At high centrifugal accelerations it was found that using the anionic polyelectrolyte PAAM/AA does not result in better dewatering performance, whereas both polycations recorded high degrees of separation. Furthermore, the measurements with the high-molar-mass PTAC indicate a high resistance to centrifugation which correlates with floc stability. In contrast, addition of the

low-molar-mass PDADMAC gives more fragile flocs, leading to faster collapse of the sludge cake in the compression zone of the centrifuge at lower gravitational forces. These experimental findings agree well with the much higher filtration capacity of sludges conditioned with PTAC which was measured by means of a pressure filtration device. Comparisons of the optimum polyelectrolyte concentrations obtained by pressure filtration or centrifugation at low gravitational forces with the zeta potential of the flocculated particles appear to be consistent with bridge formation for PTAC and with the charge patch mechanism for PDADMAC. The centrifugation experiments at high centrifugal accelerations show an optimum separation efficiency at relatively low degrees of coverage and a high level of agreement with the large-scale process.

Key words Polyelectrolytes – Flocculation – Sewage sludge – Centrifugation analyser – Zeta potential

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Introduction

Polyelectrolytes are widely used as flocculation aids to enhance the solids/liquids separation of wastewaters.

Sewage sludge from municipal effluent, for instance, consists of organic and inorganic suspended matter with a broad particle-size distribution ranging from colloidal to macroscopic dimensions. Due to charge stabilization

colloidal and even larger particles in wastewater require coagulation, for example, caused by oppositely charged polyelectrolytes, to achieve larger, faster settling flocs [1].

In Germany approximately $6 \times 10^7 \text{ m}^3$ of sewage sludge is generated every year. With an average solid content of 5% this amount corresponds to 3 million tonnes of dry substance [2]. An even larger quantity of sludge ($8 \times 10^7 \text{ m}^3$) to be disposed of can be expected for the year 2000. The sewage sludge investigated in this study is conditioned by biological cleaning as well as anaerobic digestion before the mechanical dewatering stage, which is accomplished on a large scale by processes such as belt filter pressing or centrifugation. As far as the latter is concerned, centrifugal decanters have long been used in municipal purification plants. Flocculation with cationic synthetic polyelectrolytes can successfully increase the recovery efficiency of the centrifuges to yield high solids contents in the sludge cake and clear centrates.

A number of laboratory methods and industrial scale experiments have been reported for selecting an appropriate polymer and its dosage. The use of the streaming current (SC) detector as a tool for dose control of polymeric flocculants is well known. Nitzsche and Müller [3] found that the optimum flocculant concentration results in charge neutralization in the clear effluent of the dewatering process. Dentel and Abu-Orf [4] measured the SC in the conditioned sludge and centrate, and in both cases the near-zero SC corresponds to the optimum polymer dose range. Dentel et al. [5] later reported that the residual polyelectrolyte concentration can be detected with higher accuracy by ^1H NMR spectroscopy compared to colloid titration. Eisenlauer and Horn [6, 7] developed the fibre-optic sensor technique which has proved useful for assessing the effectiveness and on-line dose control of polymeric flocculants by floc-size measurements in flowing systems [8]. Another optical method is based on a charge-coupled device (CCD) camera giving a floc-size distribution which serves as a parameter for controlling the polyelectrolyte dosage in the dewatering process [9]. Several investigations have been published on rheological measurements of flocculated sludges giving some insight into conditioning mechanisms and the structure of flocs [10–12].

All these methods either focus on the optimization of sludge conditioning prior to the mechanical dewatering stage or on the analysis of the separated liquids, but they lack parameters for evaluating the dewatering capacity on belt filter presses or centrifuges.

In our prior studies [13–15] we reported that the polyelectrolyte dosage for filtration processes of different industrial sludges can be optimized by means of a pressure filtration device [16]. This method enables the dewatering of slurries and the compression of the filter cake in belt screen presses to be simulated so that a high

level of agreement is achieved with the large-scale process [13, 14]. Similar laboratory tests have been employed by other authors to evaluate floc formation under stress conditions [17–19].

This paper describes a new method to investigate the sedimentation process in sludges and the packing behaviour of sediments by means of a centrifugation analyser with an optoelectronic measuring system [20, 21]. During centrifugation the light transmission is recorded continuously as a function of the radial position over the entire length of a cuvette filled with the sample. Integrated software determines the filling height and the position of the time-dependent supernatant/sediment interface. From these data the increasing relative length of the centrate is calculated as a function of time and is displayed as a centrifugation curve. Moreover, this apparatus allows the separation behaviour of suspensions to be analysed under the influence of various centrifugal forces (5–1000 g), and has successfully been applied in determining the red cell volume in blood [20] and the deformability of soft microcapsules [21].

Until now time-consuming laboratory tests such as the cylinder or jar test [22] have been widely used to determine the optimum concentration of polyelectrolytes for solids/liquids separation in wastewater treatment. As both are carried out under gravitational force (1 g), a simulation of the settling behaviour of particles in large-scale centrifugation processes is not possible. In continuous decanter centrifuges high gravitational accelerations of up to 2500 g can be applied [23], thus according to Stokes' law much lower retention periods should be necessary to obtain the required separation efficiency in comparison with the removal of suspended solids by sedimentation.

In this article we show that the optimum dosage level of polyelectrolytes in decanter centrifuges can be evaluated better by automatic registration of the separation process at high gravitational forces with the aid of the above-mentioned method. As an example, the solids/liquids separation of sewage sludge is investigated systematically by using polyelectrolytes of different types. Furthermore, the dewatering behaviour of the conditioned sludges is tested by means of a pressure filtration device [16]. Finally, these results are compared with zeta potential measurements in order to determine the state of particle charge required for the optimum flocculation concentration obtained by both methods.

Experimental

Suspension

The sewage sludge investigated in this paper was taken from a municipal purification plant (Klärwerk Köhlbrandhöft, Hamburg). In this plant coarse solids and sand are removed from the raw effluent by preliminary treatment using trash racks and sedimentation basins. The subsequent biological cleaning stage is carried

out by bacteria in an activated sludge tank. Nitrification occurs by specific organisms that convert ammonia and nitrite to nitrate. In a final settling tank denitrification is performed by bacteria using the combined oxygen from the nitrates thus resulting in the release of nitrogen gas. The sediments occurring in the primary and biological cleaning stages as well as in the process of nitrification/denitrification form the raw sludge. Anaerobic sludge digestion is applied to this material to yield a stabilized sewage sludge with a concentration of approximately 3% total solids. In the large-scale plant a dosage of approx. $7000 \mu\text{g} \cdot \text{g}^{-1}$ (dry substance) of a high-molar-mass cationic polyelectrolyte is added to cause flocculation. By means of decanter centrifuges the conditioned sludge is concentrated to 22% total solids which can be increased to 55% in a drying plant. This enables the final disposal as fertilizer or combustible material. The characteristic data of the sewage sludge investigated are summarized in Table 1.

Flocculation additives

The samples used were commercially available polyelectrolytes of different molar mass, density and nature of charge. Poly[acrylamide-*co*-(*N,N,N*-trimethylammoniummethylacrylate chloride)] (PTAC) was purchased from Nordmann & Rassmann (Hamburg, Germany). The high-molar-mass cationic polyacrylamide poly(diallyldimethylammonium chloride) (PDADMAC), as an example of a polycation with high charge density and relatively low molar mass, was supplied by Stockhausen (Krefeld, Germany). In addition, an anionic flocculation agent of the poly(acrylamide-*co*-acrylate) type (PAAM/AA) was also obtained from Stockhausen.

The molar masses were determined by viscometry. The measurements were performed with either a Ubbelohde-type capillary viscometer or a Zimm-Crothers rotational viscometer for the modified polyacrylamides at 25 °C. The percentages of cationic or anionic groups in the acrylamide copolymers were determined by ^{13}C NMR spectroscopy using the inverse-gated decoupling technique and ultrasonic degradation before analysis to reduce sample viscosity [24]. The analytical data of the polymers and the constants

Table 1 Characteristic data of the sewage sludge

Parameter	Value
Dry substance (%)	3.0
Loss on ignition (%)	50.4
Zeta potential (mV)	-20
Particle-size distribution (μm)	0.05 ... 1000 ^a
Salt content of dry substance (%)	< 2

^a Measurement performed with a Mastersizer S (Malvern Instruments Limited, Malvern, UK)

Table 2 Analytical data for the flocculating agents poly[acrylamide-*co*-(*N,N,N*-triethylammoniummethylacrylate chloride)] (PTAC), poly(diallyldimethylammonium chloride) (PDADMAC)

Polymer sample	$[\eta]$ (ml g^{-1})	M_η (10^3 g mol^{-1})	K_η	a	x_{ig} (mol %)
PTAC	1295 ^a	16000	1.36×10^{-3} [25]	0.83 [25]	25
PDADMAC	66 ^b	47	7.06×10^{-3} [26]	0.85 [26]	100
PAAM/AA	3400 ^c	7600	3.90×10^{-4} [27]	0.91 [27]	36

^a Determined in 1 M NaCl at 25 °C according to Ref. [25]

^b Determined in 0.1 M NaNO₃ at 25 °C according to Ref. [26]

^c Determined in 1 M NaCl at 25 °C according to Ref. [27]

of the Mark-Houwink equations (K_η , a) used for the calculation of the molar masses are given in Table 2.

Sludge conditioning procedure

In order to prepare the samples for the various experiments, an appropriate amount of sewage sludge suspension was placed in a beaker and a 0.1 or 0.2% solution of the flocculation additive was added. For the zeta potential measurements of the particles it was necessary to dilute the original sewage sludge to 0.01% of total solids.

After polyelectrolyte addition the slurry samples were stirred at a speed of 500 rpm for 1 min. It was demonstrated that neither longer stirring periods nor lower mixing energies induce a better dewatering performance.

Methods

Separation analyser (LUMiFuge)

The separation analyser (LUMiFuge, L.U.M. Berlin, Germany) allows the separation behaviour of suspensions to be determined under the influence of various centrifugal forces (5–1000 g). This apparatus is based on a low-speed centrifuge which is combined with an optoelectronic measuring system that records the light transmission over the entire sample cuvette (Fig. 1).

The cuvettes containing the suspension are positioned in the horizontal plane on the rotor of the centrifuge. During centrifugation a light source positioned above the rotor emits radiation (near-infrared) onto the sample. Transmitted light is detected by a CCD line sensor below the rotor plane and is analysed by a microcontroller which generates a light-transmission profile of the sample area for every measurement step. The transmission profile

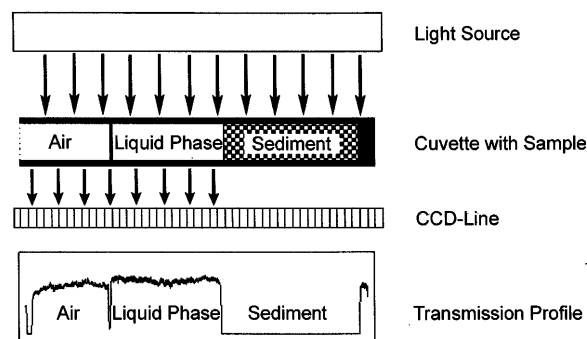


Fig. 1 Measuring principle of the separation analyser (LUMiFuge)

and poly(acrylamide-*co*-acrylate) (PAAM/AA). $[\eta]$: intrinsic viscosity, M_η : viscosity average of molar mass, K_η and a : constants of the Mark-Houwink equations, x_{ig} : percentage of ionic groups

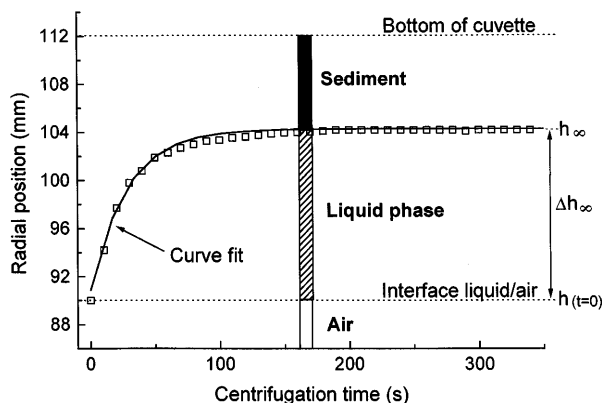


Fig. 2 Sedimentation curve fitted with an exponential function

displays the intensity of the light transmitted through the sample as a function of the radial position. By means of these profiles the software determines the radial position of the interfaces between fluid/air and sediment/particle-free fluid. The time course of the increasing length of the clear liquid phase with high transmission values can be displayed as separation curve, as shown in Fig. 2.

Fitting an exponential function to the separation curve supplies kinetic parameters for a quantification of the sedimentation process [28] dependent upon the centrifugal acceleration, the suspension characteristics as well as the type and concentration of the flocculating agent used for dewatering. The position of the interface between sediment and particle-free fluid (h_{if}) as a function of centrifugation time (t) is given by

$$h_{if} = h_{\infty} - \Delta h_{\infty} \exp(-k_c t), \quad (1)$$

where h_{∞} is the position of the solid/liquid interface, Δh_{∞} is the height of the liquid phase after an infinite separation period ($\Delta h_{\infty} = h_{\infty} - h_{(t=0)}$) and k_c is the centrifugation constant. In this study we employed the so-called time constant t_c (Eq. 2) to evaluate the centrifugation velocity which is given by

$$t_c = \frac{1}{k_c}. \quad (2)$$

At slow sedimentation velocities high values of the time constant t_c are obtained, whereas at rapid separation rates complete sedimentation is achieved after a short period of centrifugation, giving low values of t_c .

For the centrifugation measurements, the conditioned sewage sludge suspension was allowed to settle for 1 min and was then homogenized by rapid mixing in order to transfer a defined sample volume into the cuvette. Immediately before the centrifugal analysis was started, the flocculated sludge was homogenized once again by means of a test-tube shaker.

Flocculation and dewatering apparatus

This apparatus allows slurries to be conditioned with flocculation additives in a container and then for the suspension to be filtered with compressed air by means of a pressure filter unit. The filtrate is collected on a balance, which is connected to an evaluation unit that records the mass of filtrate as a function of time.

For better comparability of the recorded filtration curves we introduced the so-called dewatering index I_D which is a dimensionless numerical value. This index indicates the dewatering velocity and the amount of separated water in relation to the theoretical maximum quantity of filtrate for a given filtration period.

The sludge samples were conditioned in the pressure container of the apparatus as described above. After a resting period of 1 min, the flocculated suspension was filtered for 3 min under a pressure of 3 bar, with the filtrate being collected and recorded.

Jar test

The flocculated sludges were centrifuged at a gravitational force of 514 g for 5 min. The jar with the remaining slurry was allowed to settle for 30 min. The transmission through the supernatant liquids of the samples of both procedures was measured at 800 nm against a distilled water reference using a UV/vis spectrophotometer (Jasco Corp., Tokyo, Japan). The volumes of the sediments could not be compared because of either an insufficient settling rate (PDADMAC) or an excessive floc size (PTAC).

Zeta potential measurements

The zeta potential (ζ) of the sewage sludge particles was measured at 25 °C with a Zetasizer 3000 (Malvern Instruments, Malvern, UK) using the technique of laser Doppler anemometry. The zeta potential is related to the measured electrophoretic mobility (μ_E) by the Henry equation (Eq. 3) [29].

$$\mu_E = \frac{2\varepsilon_r \varepsilon_0 \zeta}{3\eta} f(\kappa a) \quad (3)$$

ε_r is the dielectric constant, ε_0 is the absolute permittivity of a vacuum, κ is the Debye-Hückel parameter and a is the particle radius. The electrophoretic measurements were made in aqueous media and at moderate electrolyte concentrations. In this case the Henry function $f(\kappa a)$ approaches the value 1.5 (Smoluchowski approximation [30], Eq. 4) corresponding to particles much larger than the double-layer thickness.

$$\mu_E = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta} \quad (4)$$

After addition of the polyelectrolyte solution and mixing, the flocculated suspension was transferred to the electrophoresis cell and the measurement was started immediately.

Results and discussion

Measurements of centrifugal separation velocity and packing behaviour

At the beginning of the investigations the influence of various polyelectrolytes on the centrifugal behaviour of flocculated sewage sludges was measured by means of the LUMiFuge separation analyser. The sedimentation curves of sewage sludges conditioned with 5000 $\mu\text{g} \cdot \text{g}^{-1}$ (dry substance) of different flocculation additives compared with the unconditioned suspension at a constant gravitational force (514 g) are shown in Fig. 3.

Conditioning of sludge samples with the anionic PAAM/AA results in a separation behaviour as for the unconditioned material, with no complete solids/liquids separation being achieved even after 30 min of centrifugation. Thus addition of PAAM/AA to sewage sludge causes no flocculation of the negatively charged colloidal particles. The use of cationic flocculation additives brings about almost complete separation of the solids

within approximately 3 min of centrifugation. Despite their different structures (replot unit, molar mass and charge density) it appears that a similar separation behaviour is indicated for both cationic flocculation additives.

Experiments to determine the influence of centrifugal acceleration on the separation behaviour were carried out at a constant dosage of $5000 \mu\text{g} \cdot \text{g}^{-1}$ for the cationic polyelectrolyte PTAC. The sedimentation curves of flocculated sewage sludges at various gravitational forces are shown in Fig. 4. Depending on the centrifugal acceleration, different sediment heights are obtained after different separation periods. The centrifugation time course allows conclusions to be drawn about the packing behaviour of the sedimented solids. At high centrifugal accelerations ($> 289 \text{ g}$) the sediment heights

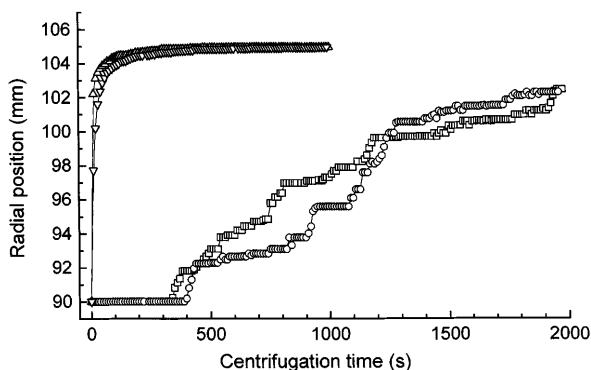


Fig. 3 Sedimentation curves of unconditioned (\square) and sewage sludges conditioned with $5000 \mu\text{g} \cdot \text{g}^{-1}$ of different flocculation additives at a constant centrifugal acceleration (514 g): poly(acrylamide-co-acrylate) (*PAAM/AA*) (\circ), poly[acrylamide-co-(*N,N,N*-trimethylammoniummethylacrylate chloride)] (*PTAC*) (\triangle) and poly(diallyldimethylammonium chloride) (*PDADMAC*) (∇). Influence of the charge nature of the polyelectrolytes on the separation velocity

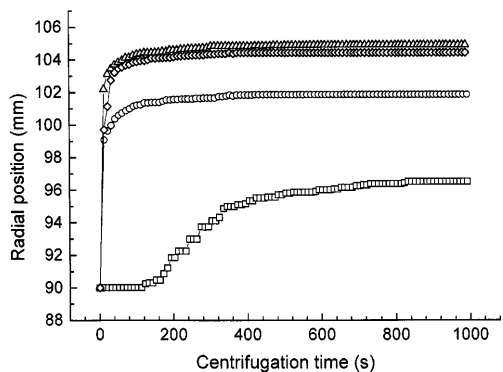
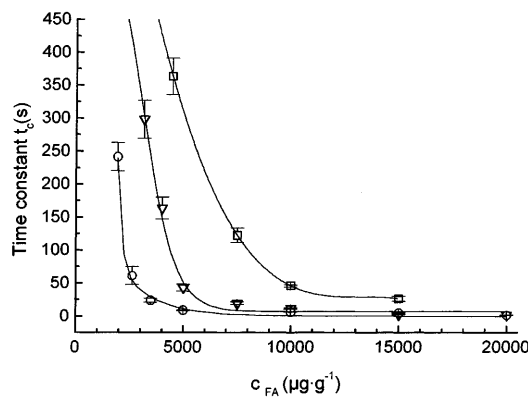
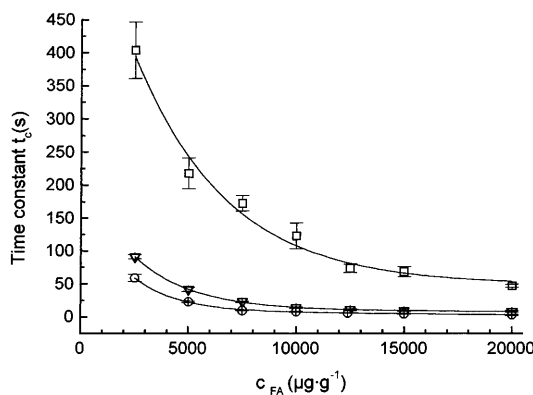


Fig. 4 Sedimentation curves of sewage sludge conditioned with $5000 \mu\text{g} \cdot \text{g}^{-1}$ of the high-molar-mass polyelectrolyte PTAC. Influence of different centrifugal accelerations on the separation velocity and sediment heights: 20 g (\square), 128 g (\circ), 289 g (\diamond) and 514 g (\triangle)



A



B

Fig. 5 Time constants, t_c , obtained by fitting the sedimentation curves of conditioned sewage sludge versus concentration of cationic flocculation additives: **A** PTAC, **B** PDADMAC. Influence of the centrifugal acceleration [(20 g (\square), 128 g (∇), 514 g (\circ))] on the separation velocity for a broad range of polyelectrolyte dosages. The mean values and standard deviations of no less than five measurements are plotted

become indistinguishable and maximum compression of the sludge cake is achieved.

For both cationic flocculation additives (PTAC, PDADMAC) sedimentation curves were recorded over a broad range of polyelectrolyte dosages in order to determine the optimum concentration for various centrifugal accelerations (20 , 128 and 514 g). Figure 5 shows time constants for the centrifugation process which were calculated according to Eq. (2) plotted against the dosages of the flocculation additive.

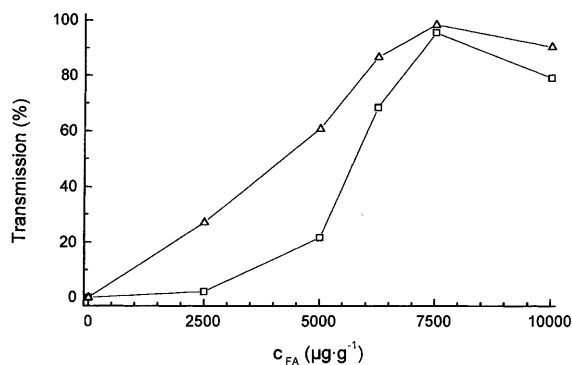
With increasing polymer concentration and centrifugal acceleration the separation velocity increases, and hence lower values of t_c are obtained. For a given centrifugal acceleration no significant increase in separation velocity can be achieved above a certain polyelectrolyte dosage and so the time constants tend towards a limiting value. At a low centrifugal acceleration of 20 g , time constants of approximately 26 s (at

15 000 $\mu\text{g} \cdot \text{g}^{-1}$) were obtained in the plateau region for PTAC and of 47 s (at 20 000 $\mu\text{g} \cdot \text{g}^{-1}$) for PDADMAC. The lower t_c values in the case of the higher-molar-mass polycation PTAC might be due to larger flocs. In general high separation velocities occur at higher centrifugal forces (128 and 514 g) by addition of both cationic polyelectrolytes despite their extremely different molar masses. In the case of the low-molar-mass PDADMAC the plateau zone of the time constant is reached at even lower polyelectrolyte concentrations than for PTAC at a moderate acceleration of 128 g. At the highest centrifugal force employed (514 g) plateau values of t_c are obtained with dosages of approximately 5000 $\mu\text{g} \cdot \text{g}^{-1}$ of both flocculation additives. The experimental data suggest that the t_c values are mainly influenced by the floc size at low centrifugal accelerations, whereas in the case of high gravitational forces the formation of smaller flocs (PDADMAC) also results in high degrees of separation at low polymer concentrations. Moreover, low t_c values at high rotational speeds indicate that the resistance to centrifugation is lower due to insufficient floc stability. Therefore, a maximum compression of the sludge cake (h_∞ value, see Eq. 1) can be obtained at lower centrifugal accelerations by addition of the low-molar-mass PDADMAC.

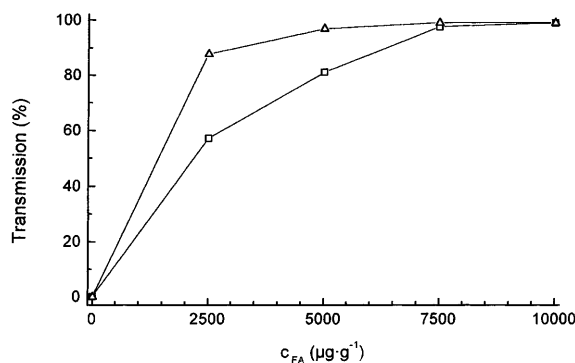
The experiments lead to the conclusion that the dewaterability of sewage sludge in decanter centrifuges can be predicted by means of the new centrifugation analyser. A polyelectrolyte can be selected by evaluating its optimum concentration. The results obtained are found to agree well with those of the large-scale process since this method supplies information about both the separation velocity and the packing behaviour of the sludge cake which correlates with floc stability in the compression zone of the centrifuge.

In addition, turbidity measurements can be carried out simultaneously with the apparatus described in order to control the centrate quality. Values for light transmission (at $\lambda = 800$ nm) through the supernatant liquid of sewage sludge samples conditioned with various dosages of polyelectrolytes (PTAC, PDADMAC) are shown in Fig. 6.

It is apparent from the data that only considering the residual turbidity obtained in the jar settling test (1 g) is not a suitable means of evaluating optimum flocculant concentrations for large-scale centrifuges. At a centrifugal acceleration of 514 g distinctly higher values of light transmission are obtained with low polyelectrolyte dosages in comparison with the jar test. Moreover, there is no need to aim for total recovery of the suspended solids in most of the sewage sludge purification plants. The jar test affords additional measurements of the centrate quality in the full-scale process. Furthermore, the recording of the sedimentation velocity obtained from the interface between supernatant liquid and the settling solids (jar test) is time-consuming and does not



A



B

Fig. 6 Light transmission ($\lambda = 800$ nm) through the supernatant liquid of conditioned sewage sludges versus concentration of **A** PTAC and **B** PDADMAC after 30 min of settling [1 g (\square)] and 5 min of centrifugation [514 g (Δ)]

allow the separation rate and floc strength to be predicted at high centrifugal forces.

Comparison of centrifugal separation with filtration and interfacial behaviour

Filtration experiments of flocculated sewage sludges have been carried out by means of the pressure filtration device [16]. As should be expected from the centrifugation results (see Fig. 3) addition of the anionic flocculation additive PAAM/AA does not improve the dewaterability of sewage sludge. The values of the dewatering index I_D in Fig. 7 indicate that the cationic polyelectrolytes PTAC and PDADMAC show different efficiencies as filtration aids. PTAC with the high molar mass and medium charge density shows its greatest dewatering efficiency at a dosage of approximately 20 000 $\mu\text{g} \cdot \text{g}^{-1}$ where a dewatering index of 90 was obtained (Fig. 7A). In contrast, for PDADMAC as a polyelectrolyte of relatively low molecular mass and high charge density a maximum dewatering index of 33 can be determined at a concentration of approximately 14 500 $\mu\text{g} \cdot \text{g}^{-1}$ (Fig. 7B).

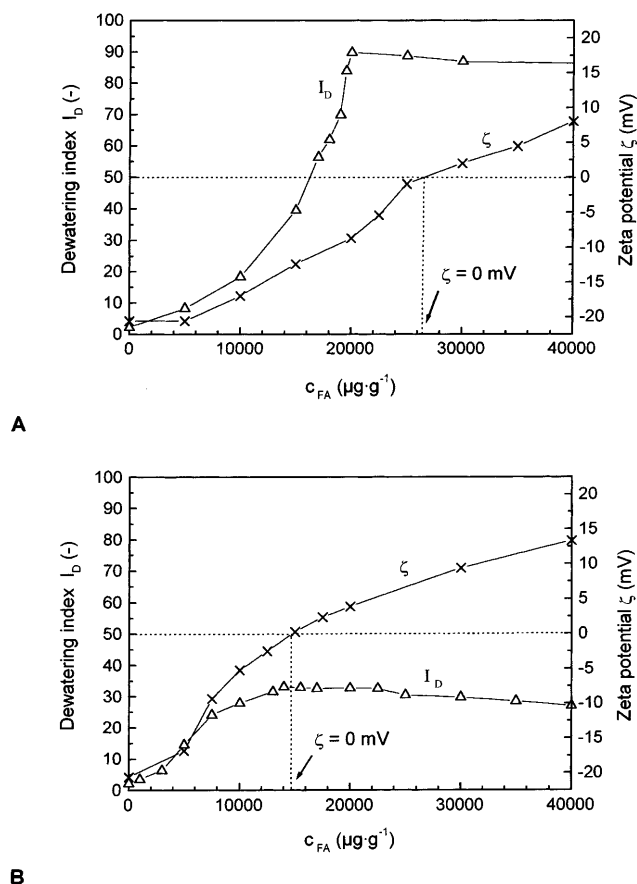


Fig. 7 Dewatering index I_D (Δ) obtained by filtration curves and zeta potential ζ (\times) of conditioned sewage sludge versus concentration of cationic flocculation additives: **A** PTAC, **B** PDADMAC. Comparison of filtration behaviour with the zeta potential of the flocculated particles

Based on these data, we conclude that the shear forces in the apparatus employed caused rapid floc erosion and increased blinding during filtration in the case of the low-molar-mass PDADMAC. The fact that sludges flocculated with PTAC can be significantly better filtered might be due to the larger and loosely packed flocs with a higher stability that are exposed to a controlled collapse of the cake in the compression zone. The experimental results are consistent with the assumptions for different floc strengths deduced from centrifugation measurements with the polyelectrolytes employed.

Zeta potential measurements of the flocculated particles were carried out (Fig. 7) in order to determine the type of particle charge required for the optimum flocculant dose. For the high-molar-mass PTAC comparison of the zeta potential data with the dewatering index (Fig. 7A) indicates a flocculation mechanism in line with the bridging model. A broad adsorption layer

on the colloid surface is thus postulated; this has a number of loops and tails extending into the liquid phase to allow bridge formation between adjacent particles. According to theoretical calculations [31, 32] effective bridging only occurs when the fraction of the surface covered by polyelectrolytes is 0.5 or even less. Experimental data confirm the assumption made for this model that complete charge neutralization for the optimum dewatering capacity is not required. At a dosage of $20\,000\ \mu\text{g}\cdot\text{g}^{-1}$ PTAC a zeta potential of $\zeta = -8.7\ \text{mV}$ is observed, whereas the point of zero charge is reached at approximately $27\,000\ \mu\text{g}\cdot\text{g}^{-1}$.

The use of PDADMAC with a relatively low molar mass and a high charge density affords a dosage of approximately $14\,500\ \mu\text{g}\cdot\text{g}^{-1}$ for the maximum value of the dewatering index ($I_E = 33$), where complete charge neutralization ($\zeta = 0\ \text{mV}$) is observed. This appears to be consistent with the electrostatic patch mechanism that assumes a flat adsorption layer of polyelectrolyte chains forming a charge mosaic on the particle surface [33]; thus, the electrostatic attraction of oppositely charged regions between adjacent particles brings about flocculation. Our prior investigations [14, 34] into the influence of molar mass on the flocculation mechanism of sewage sludge, which were carried out with a homologous series of PDADMAC samples, support the mechanistic assumptions described here. With the low-molar-mass PDADMAC samples ($M_n = 5000$ and $100\,000\ \text{g}\ \text{mol}^{-1}$) agreement has been found between the dosage rates for $\zeta = 0$ and for the optimum dewatering capacity. In the case of the PDADMAC with the highest molecular weight ($M_n = 411\,000\ \text{g}\ \text{mol}^{-1}$), the optimum concentration is significantly lower than the amount required for the point of zero charge. Furthermore, it is postulated for the charge patch model that with increasing ionic strength the additional attraction of the particles decreases and thus the flocculation efficiency is diminished. Due to the given salt content of the sewage this aspect was not investigated in detail.

Finally, slightly higher polyelectrolyte concentrations above the optimum dosage rates do not result in a considerable decrease in the dewatering index I_D . Therefore, we suggest that a partial charge reversal of the particles, which is indicated by the zeta potential, does not lead to significant impairment of the filtration behaviour in the dosage range investigated.

Table 3 summarizes the optimum polyelectrolyte concentrations obtained by centrifugation experiments at high (514 g) and low (20 g) gravitational forces and by pressure filtration tests which are compared with the amount required for complete surface charge neutralization ($\zeta = 0\ \text{mV}$).

A comparison of the data indicates that for high separation efficiencies in filtration and centrifugation at low gravitational forces with PDADMAC surface charge neutralization is required according to the charge patch

Table 3 Optimum polyelectrolyte dosages obtained by centrifugation ($t_{c,\min}$) and filtration ($I_{D,\max}$) experiments in comparison to the amount required for the point of zero charge ($\zeta = 0$ mV)

	Concentration of flocculation additive c_{FA} ($\mu\text{g} \cdot \text{g}^{-1}$)			
	$t_{c,\min}$ (514 g)	$t_{c,\min}$ (20 g)	$I_{D,\max}$ (3 bar)	$\zeta = 0$ mV
PTAC	~ 5000	~ 10 000	20 000	27 000
PDADMAC	~ 5000	~ 12 500	13 000	14 500

model. In contrast, the optimum dosage of PTAC for these processes lies far below the concentration at which the point of zero charge is reached. At high centrifugal accelerations low degrees of coverage are needed to achieve sufficiently high separation rates for both polyelectrolytes. Moreover, from the measured dewatering efficiencies we conclude that flocculation by the charge patch mechanism produces agglomerates of smaller size and poorer stability than bridging formation.

Conclusions

A new method for the optimization of the polyelectrolyte dosage in centrifugal solids/liquids separation of wastewater treatment sludges was introduced. The centrifugation analyser employed in this study is based on a low-speed centrifuge with an optoelectronic sensor which records the position of the sediment/fluid interface as a function of the separation time. As a result, sedimentation curves can be obtained which supply parameters for the separation velocity as well as for the packing behaviour after a certain period. Therefore, we were able to determine the optimum concentration of different polyelectrolytes in centrifugation processes at various gravitational forces. Even at high centrifugal acceleration (514 g) the use of the anionic polyacrylamide PAAM/AA does not result in a significant improvement in the separation process, whereas with cationic flocculation additives (PTAC, PDADMAC) nearly complete separation can be obtained within a short centrifugation time. Moreover, the resistance of the sludge cake to centrifugal forces was found to be higher for PTAC. The results indicate that a high molar

mass is an important factor for sufficient floc stability. Experiments performed with a pressure filtration device show that the effectiveness of the low-molar-mass PDADMAC in filtration processes is much less than that of the cationic polyacrylamide. It is apparent that rapid floc erosion and increased blinding during filtration is caused in the case of the low-molar-mass PDADMAC due to low floc stability. Larger and loosely packing flocs of higher stability might be responsible for the significantly better filtering performance of sludges flocculated with PTAC.

The results of the centrifugation analyses and the pressure filtration tests were compared with the zeta potential of the flocculated particles over a wide range of polyelectrolyte concentrations. It was found that the optimum dosage level of PDADMAC in the case of low centrifugal accelerations and filtration measurements occurs at the point of zero charge, which is consistent with the charge patch mechanism, whereas the experimental data for the cationic polyacrylamide indicate a bridge formation. At high centrifugal accelerations only a relatively low degree of coverage is required for both cationic polyelectrolytes to obtain high separation efficiencies. Thus, with the method described a better evaluation of the polyelectrolyte dosage for large-scale centrifugation processes can be obtained than with conventional methods, for example, the jar test.

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