EFFECT OF ORGANIC POLYELECTROLYTES ON SEDIMENTATION PROPERTIES OF POST-COAGULATION SLUDGE

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Abstract
A study was carried out into sedimentation of sludge obtained in the process of coagulation-flocculation of pulp and paper wastewater with the use of PAC and organic polymers. An attempt was made to evaluate the effect of various organic polyelectrolytes on phase separation effectiveness. It was found that the application of cationic polymers at a dose of 1 mg dm$^{-3}$ and 1.5 mg dm$^{-3}$ (Z 63 and Z 92, respectively) in combination with PAC had a positive effect on the reduction in the sludge volume when compared with the sludge volume obtained in the process of coagulation with PAC without a flocculant. It was also noted that following the application of the optimum dose of either cationic or anionic polymers the sedimentation period was considerably reduced from 60 min (sample without flocculants) to even 30–35 min.
Introduction

Chemical engineering deals, among others, with the removal of dissolved substances and particles of various sizes from water and wastewater. Depending on their size, particles can be removed mechanically (particles > 1 mm) or through sedimentation (particles > 100 μm). In the case of particles smaller than 1 μm this problem can be solved by the application of processes resulting in the aggregation of solid substances dispersed in water or wastewater, with a significant effect on sedimentation and filtration efficiency. Chemical coagulation and flocculation of particles are considered common effective aggregation techniques. The process of flocculation is widely applied in various branches of industry, including wastewater treatment. Increasing volumes of sludge constitute a significant problem for sludge management and possible methods of utilisation (BARAN, TURSKI 1999). Synthetic organic polymers find application in liquid-solid phase separation on an industrial scale. Combinations of inorganic coagulant and synthetic organic polymers as flocculating agents are used in order to improve the process efficiency. The main task of a flocculant is to improve stabilisation of flocs and separate them in the form of post-coagulation sludge. Considerably large molecular weights of flocculants enhance the formation of large flocs with better structure and resistance to damage. Active sites to be found along the polymer chain may bind to several particles at the same time and initiate their aggregation. The flocculation process induced by the bridge formation within the macromolecular polymers is the most effective way to produce large flocs. Both the size and the density of the resulting aggregates have a significant effect on the effectiveness of phase separation during, among others, sedimentation or filtration. Polyelectrolyte type and the adsorbed polymer chain conformation are the key factors in the flocculation mechanism (GREGORY 2009). The optimum flocculation occurs when the polyelectrolyte chains extend in the form of ribbons, adsorb themselves onto the particles; surfaces and form polymer bridges.
The macromolecular chain extends as the degree of hydrolysis of the anionic polymer increases (SASTRY 1999). The macromolecular conformation also depends on the polymer charge density. Electrostatic interactions between the particular polymer segments, especially between those with high charge density, unfold the macroion ribbon. According to BOLTO and GREGORY (2007), hydrodynamic conditions (stirring, diffusion) can also essentially affect the polymer adsorption degree, especially those of higher molecular weights. Organic polymers should be added in the optimum dose. If the dose is too low, the bridging is insufficient and, in consequence, the flocculation is inefficient. The application of organic polyelectrolytes offers many benefits such as high efficiency at low doses, reduction in the required dose of inorganic coagulant and considerably higher cost-effectiveness of treatment (approx. 25–30% lower costs) (NOZAIC 2001). Organic polymers are also less affected by pH changes.

The effectiveness of the entire technological process is determined by the effectiveness of flocculation and phase separation in a system. The aim of the presented study was to determine the effect of the ionic character of organic polymers on the phase separation in the process of coagulation/flocculation with PAC (poly-aluminium chlorides).

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**Material and Methods**

PAC (poly-aluminium chloride), made up of 47–52 mg Al dm$^{-3}$ and c.a. 97 g Ca$^{2+}$ dm$^{-3}$, was used as a coagulating agent. The process of coagulation/flocculation was performed in the presence of various high molecular weight organic polymers, both cationic (Z 63 and Z 92) and anionic (M 1011 and P 2540).

Chemical coagulation of wastewater was carried out following a standard jar-test procedure:
- fast stirring (400 rpm) – 1 min,
- slow stirring (30 rpm) – 15 min,

Following the fast stirring period, measurements of the volume of the sediment sludge were performed every 5–10 min for 1 h. Such a period was sufficient to complete the sedimentation process.

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**Results and Discussion**

The effectiveness of sedimentation is determined, among others, by particle type, their size, degree of hydration and the time of their sedimentation.
Sedimentation curves $I_S = f(t)$ were plotted in order to determine the sedimentation parameters. The sedimentation index ($I_S$) defines gains in sludge volume over time ($V t^{-1}$ [cm$^3$ min$^{-1}$]). Figures 1a–d present the sedimentation curves of sludge obtained with the application of inorganic coagulant (PAC) and organic polymers of various ionic character in 1 h. The flocculants were added in doses ranging from 0.5–1.5 mg dm$^{-3}$. Power curve and $R^2$ ($R^2 > 0.96$) equations are given under each curve.

Figure 1a presents the effect of P 2540 polymer on the sludge sedimentation process. The resulting flocs fell at varied rates and formed sludge layers of various thickness. P 2540 polymer doses from 0.5–1.5 mg dm$^{-3}$ reduced $I_S = 0.258–0.3$ cm$^3$ min$^{-1}$ (after 60 min) when compared with $I_S = 0.4$ cm$^3$ min$^{-1}$ obtained with the use of PAC (without flocculants). When comparing the sedimentation curves of the sludge produced with organic flocculants (Figures 1a–d), it was found that the $I_S$ values obtained (after 60 min) were considerably lower for Z 63 ($I_S = 0.18–0.26$ cm$^3$ min$^{-1}$) and Z 92 ($I_S = 0.25–0.29$ cm$^3$ min$^{-1}$) than for P 2540 and M 1011 ($I_S = 0.26–0.3$ cm$^3$ min$^{-1}$). The smallest gain in the sludge volume over times of $I_S = 0.18$ cm$^3$ min$^{-1}$ and $I_S = 0.25$ cm$^3$ min$^{-1}$ were observed for a 1 mg dm$^{-3}$ dose of Z 63 a 1.5 mg dm$^{-3}$ dose of Z 92, respectively. Differences in the $I_S$ values and in the course of sedimentation curves obtained in the sedimentation with inorganic coagulant and organic polymers may indicate a change in the particle aggregation degree. The obtained $I_S$ values also indicate the great effect of cationic flocculants on sludge sedimentation and a diversified aggregation mechanism. However, during visual observations of the flocculation process, an aiding capacity of flocculants in the formation of flocs of greater sizes was reported, especially for P 2540 and M 1011. This can be caused by the greater hydration degree of these flocs. The colloidal particles may have been agglomerated directly by the flocculant particles. It could be concluded that the slowly falling flocs were more hydrated than those falling faster.

Interactions of organic polymers with inorganic coagulants produce more stable flocs than those obtained with coagulants used alone (GREGORY and LI 2004). The application of organic polymers produces larger flocs up to a certain limit. When this limit is reached, the flocs disintegrate into several smaller parts. Sedimentation curves reflect the differences in the activity of flocculants with various ionic characters. The results show that both the ionic character and the applied dose of a polymer significantly affect the resulting sludge volume.

Figure 2 characteristics of sludge sedimentation with 15 mg dm$^{-3}$ PAC and anionic flocculants.
Fig. 1. Sludge volume gain over time during coagulation with 15 mg dm$^{-3}$ PAC and $a$, $b$ – anionic, $c$, $d$ – cationic polymer
Figure 2 presents the separation characteristics of flocs with 15 mg dm$^{-3}$ PAC and selected doses of anionic flocculants. It was found that the doses of 0.5 mg dm$^{-3}$ and 1.5 mg dm$^{-3}$ of P 2540 flocculant ensure a reduction in the sludge volume by 27% and 37%, respectively. The fall time of the flocs obtained with P 2540 was shortened from 60 (only PAC) to about 30–45 min. A similar result was obtained with an anionic flocculant – M 1011. The highest applied doses of 1.5 mg dm$^{-3}$ was found to be optimal. However, the resulting flocs fell slightly slower than those obtained with the cationic flocculants. It could be assumed that these flocs were hydrated to a greater degree. The entire sedimentation process was completed in periods from 35 min (1.5 mg dm$^{-3}$) to 45 min (1 mg dm$^{-3}$). Other authors (ØDEGAARD 1992) reported that the application of PAC results in the formation of flocs with a predominating local positive charge which can potentially serve as a site of flocculant particle bonding.

Figure 3 shows characteristics of sludge sedimentation with 15 mg dm$^{-3}$ PAC and cationic flocculants.
The data presented in Figure 3 show the sludge sedimentation effect obtained in the coagulation/flocculation of pulp and paper wastewater with 15 mg Al dm$^{-3}$ (PAC) and the most effective doses of cationic flocculants. In all cases, the flocs’ falling process was completed within 30–35 min. An addition of 1–1.5 mg dm$^{-3}$ of Z 92 flocculant resulted in the reduction of sludge volume by 35–39% compared to a control sample (only coagulant). The highest effectiveness in sludge volume reduction, however, was obtained with the Z 63 cationic polymer. The optimum dose of 1.5 mg dm$^{-3}$ reduced the volume of solid phase by 55.1% when compared with the control sample. The reduction in the sedimentation time by half (when compared with the samples treated only PAC) indicates the high effectiveness of both Z 92 and Z 63 flocculants. Due to their adsorption and bridging properties, polymers may enhance orthokinetic flocculation (KOWAL 2009).

Cationic flocculants have a destabilising activity due to the adsorption processes, charge neutralising and bridging by polymers. Simple anions and polycations are produced in the process of dissociation of a cationic polyelectrolyte in water. Organic polycation activity is similar to that of polyhydroxyca-
tions of a coagulant, therefore, cationic polymers act similar to flocculants and coagulants applied together (ØDEGAARD et al. 1992).
The 35–55% reduction in the sludge volume obtained with cationic floc-
culants Z 92 and Z 63 was more beneficial than the 27–37% reduction reported
for anionic floculants P 2540 and M 1011. Similar results, i.e. a 42%-reduction
in sludge volume obtained in the coagulation of breeding farm wastewater with
anionic PAA applied in combination with FeSO₄ were obtained by Aguilar et al.
(2005). Generally, the application of both the anionic and cationic flocculants
in combination with PAC had a positive effect on the reduction of sedimenta-
tion time by approx. 40–50%. Both the cationic and anionic (floculants
ensured greater packing of sludge flocs by forming {Al(OH)_3}-{org}-{cationic
floculant}-type and {anionic floculant}-{Al(OH)_3}-{org})-type structures
which were more compact than the {Al(OH)_3}-{org} structures (without
floculant).

Wastewater particles with predominating negative surface charge (DEN-
tel, Gosset 1987) are destabilised by cationic organic flocculants through
charge neutralisation, while anionic flocculants may initiate bridging, which
could explain the slightly lower effectiveness of anionic flocculants when
compared to cationic ones.

Based on the above results, it appears that the application of an inorganic
coagulant in combination with a cationic organic flocculant such as Z 92 and
Z 63 ensures a better flocs separation characteristic for pulp and paper
wastewater. At the optimum dose of an inorganic coagulant, only a small
addition of flocculant to a large degree reduced the sludge volume. In the
present study, an increase in the sludge volume over that obtained in the
control sample was not observed.

The reduction in the solid phase volume and the time of phase separation
following a coagulation serves as a measure of efficient activity of a coagulant-
floculant system. Both a coagulant and a flocculant should be applied in
optimum doses when used in combination. Excessive doses of coagulants may
produce larger sludge volumes and reduced efficiency of the process. The
application of optimum doses of a coagulant-flocculant pair ensures cost-
efficiency and ecologically-friendly results.

Flocculant doses are much smaller than those of coagulants and practically
do not usually exceed 2 mg dm⁻³. However, for the currently reported high
wastewater loads, the application of flocculants without an inorganic coagulant
is not recommended for economic reasons.

Conclusions

1. Both the cationic and anionic flocculants considerably enhance the
sedimentation of flocs produced in the coagulation process.
2. The best characteristic of phase separation was recorded for Z 63, whose 1 mg dm$^{-3}$ dose reduced the sludge volume gain to the largest degree, i.e. to $I_S = 0.18$ cm$^3$ min$^{-1}$. An addition of cationic organic flocculants to inorganic coagulant decreased this value to $I_S = 0.4$ cm$^3$ min$^{-1}$ (for PAC), $I_S = 0.18$–$0.26$ cm$^3$ min$^{-1}$ (for Z 63) and $I_S = 0.25$–$0.29$ cm$^3$ min$^{-1}$ (for Z 92).

3. The applied anionic polyelectrolytes had a positive effect on phase separation, however, this influence was not as strong as that exerted by cationic polyelectrolytes. When applied in combination with PAC, P 2540 and M 1011 produced $I_S = 0.258$–$0.3$ cm$^3$ min$^{-1}$ and $I_S = 0.266$–$0.3$ cm$^3$ min$^{-1}$, respectively.

4. The obtained value of $I_S = 0.258$–$0.3$ cm$^3$ min$^{-1}$ following the application of P 2540 and $I_S = 0.266$–$0.3$ cm$^3$ min$^{-1}$ for M 1011 also had a positive effect on phase separation but not to as high a degree as the cationic flocculants.

5. The application of PAC in combination with cationic (Z 63 and Z 92, at a dose of 1–1.5 mg dm$^{-3}$) and anionic (1.5 mg dm$^{-3}$ P2540 and 1–1.5 mg dm$^{-3}$ M 1011) flocculants shortened the sedimentation time to 30–35 min when compared with the samples with only an inorganic coagulant.

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