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COMPARISON OF SEDIMENTATION TESTS OF WASTEWATER SLUDGE AND AGGREGATES OF MODEL SILICA SUSPENSION

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A b s t r a c t

Results of sedimentation tests conducted on pulp and paper wastewater were compared with the results of macroscopic photographic analysis of silica aggregate suspensions. The peak effectiveness of the phase separation was achieved with the use of cationic polymer Z63 which – when used together with polyaluminium chloride (PAC) – reduced the volume of sludge by up to 38% compared to PAC alone. Used together with anionic (P2540, M1011) and cationic (Z63, Z92) polymers, PAC reduced the sludge sedimentation time by half compared to PAC alone. Aggregates formed during the process of silica flocculation with PAC and cationic flocculant Z63 are larger than those formed with an anionic one.

PORÓWNANIE TESTÓW SEDYMENTACJI OSADU ŚCIEKOWEGO Z AGREGATAMI MODELOWEJ ZAWIESINY KRZEMIONKI

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S ł o w a k l u c z o w e: flokulacja, sedymentacja, polimery organiczne.

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A b s t r a k t

Porównano wyniki testów sedymentacyjnych przeprowadzonych na ściekach celulozowo-papierniczych z wynikami makroskopowej analizy fotograficznej agregatów zawiesiny krzemionki. Najwyższą skuteczność separacji faz uzyskano z udziałem polimeru kationowego Z63, który we współpracy z chlorkiem poliglinu (PAC) obniżał objętość warstwy osadu ściekowego nawet do 38% w stosunku do samego PAC. PAC zarówno we współpracy z polimerami anionowymi (P2540, M1011), jak i kationowymi (Z63, Z92), powodował skrócenie czasu sedymentacji osadu ściekowego o połowę w porównaniu z próbami z samym PAC. Agregaty utworzone w procesie flokulacji zawiesiny krzemionki za pomocą PAC i kationowego flokulantu Z63 charakteryzują się wyższym wymiarem niż te otrzymane z flokulantem anionowym.

Introduction

There are currently a number of methods used to determine the degree of particle aggregation (GREGORY 2009, YU et al. 2006), which enable analysing the kinetics of aggregation and change of the size of floccules formed at different stages of flocculation. Kinetics of the particle aggregation can be described by either of two models. The model of perikinetic particle collisions, associated with Brownian motion, can be applied to particles smaller than 1 μm. On the other hand, orthokinetic aggregation, caused by hydrodynamic interactions (for example while suspension is being stirred) occurs for particles larger than 1 μm. According to GREGORY (2009), the number of particles decreases in a linear manner in the process of orthokinetic aggregation and it does so exponentially during the process of perikinetic flocculation. A similar degree of aggregation can probably be achieved over a slightly longer time as a result of orthokinetic flocculation compared to the perikinetic process. The process of orthokinetic flocculation results in the formation of open-structure floccules. Particle collisions according to the CCA (cluster-cluster aggregation) mode result in the formation of floccules of different sizes. The aggregation model proposed by MEAKIN and KOLBE (1983) assumes collisions of monodispersive particles, which join and form e.g. dimers which can bind with other dimers or with individual particles. Such a process leads to the formation of aggregates of different shapes and a wide range of sizes. The effectiveness of particle aggregation in the process of flocculation with the use of polyelectrolytes depends mainly on the conditions of stirring, degree of polymer adsorption on particles and re-conformation of the polymer chain.

The effectiveness of water and wastewater purification with inorganic coagulants may increase as a result of the use of organic polyelectrolytes. The most frequently used ones include acrylamide copolymers, whose chains can change their conformation and stretching during the process of hydrolysis. The degree of polymer hydrolysis largely depends on the polymer charge density and pH of the environment (BOLTO 1995). NAPPER (1983) proposed a model of polymer adsorption in three forms of contact with the adsorbing surface: trains, tails and loops. There is a great diversity of opinions on the minimum coverage of the particle surface with polymer, which is necessary for effective flocculation to take place. The results of research conducted by DAS and SOMASUNDARAN (2004) show that the degree of effective flocculation when ultra-low doses of macromolecular PAA are used is three times lower than is needed for covering them with a monolayer of the polymer.

Anionic flocculants are regarded as the most effective polymers in the process of wastewater purification because of the presence of weakly anionic carboxylic groups in them. The maximum carboxylation of 10% is achieved in processes of electrochemical carboxylation of copolymers of acrylic acid (BOLTO 1995). The use of organic polyelectrolytes brings several benefits: they reduce doses of inorganic coagulants and favour a decrease in the amount of sludge, they also ensure a lower level of Al residue in water; and they are less dependent on pH changes.

Using excessively large doses of polymers results in numerous problems, such as re-dispersion of impurities, while using insufficient doses results in ineffective coagulation, which manifests itself in a high level of suspension and colour in purified water BOLTO (1995). The aim of the study was to compare the sedimentation rate of sludge and the results of the macroscopic photographic method of aggregates from the suspension $(SiO_2)_n$ formed by coagulation of pulp and paper wastewater and a model silica system. Coagulation/flocculation was conducted with the use of PAC and organic flocculants with a diverse ionic character.

Methods

The effect was investigated of organic polymers with various ionic features used together with PAC on the process of phase separation in the coagulation/flocculation of pulp and paper wastewater. Table 1 presented the characteristic of pulp and paper wastewater before and after coagulation by PAC.

Table 1

Characteristic of pulp and paper wastewater before and after coagulation by PAC

Dose PAC [mg Al dm^{-3}]	Turbidity	COD	Suspended solid	Colour
	[mg dm^{-3}]			
0.0	860	1754	680	4680
20	34	788	14	179

A comparative analysis of the effectiveness of selected organic flocculants (anionic P2540 and M1011 and cationic Z63 and Z92) was conducted. After the process of coagulation/flocculation was completed, the increase in the sludge layer over 1 hour was measured.

A macroscopic photographic method (WIERZBICKA 2000) was used in order to measure the size of floccules formed by coagulation of the model suspension of silica with inorganic coagulants with the addition of some organic flocculants. The most effective flocculants were selected: anionic P2540 and cationic Z63. Aggregates of the appropriate sludges were measured in magnification x36 and the actual distribution of floccule sizes was determined based on those values. Each of the sludges are characterised by a diagram $Z(\%) = f(R)$, Z (%) – distribution of floccule sizes, R – size of object.

Results and Discussion

The effectiveness of flocculation was expressed as the volume of sludge formed over 60 minutes. Figure 1 and Figure 2 show the process of phase separation caused by orthokinetic flocculation conducted with 20 mg of Al dm^{-3} with PAC used together with cationic and anionic organic flocculants.

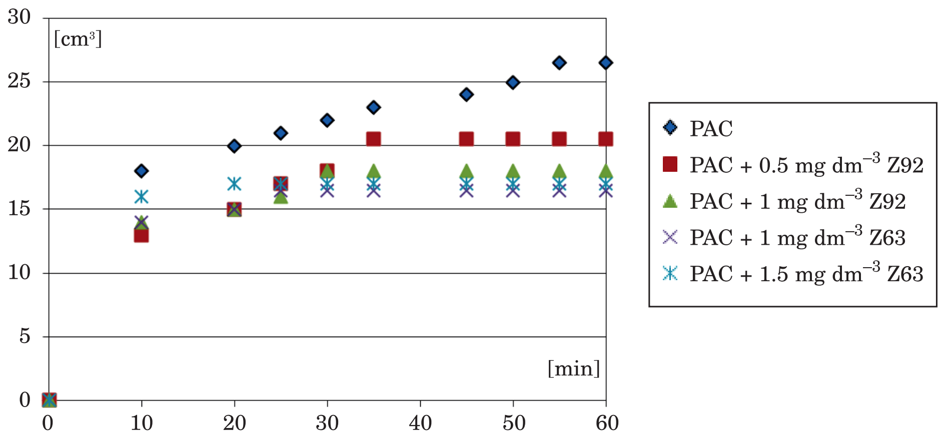

Fig. 1. Characteristics of the sludge sedimentation using PAC and cationic polymers

The diagrams show that the highest effectiveness in the phase separation process was achieved with the cationic polyelectrolyte Z63, whose dose of 1 and 1.5 mg dm^{-3} reduced the solid phase by 38% and 36% compared to PAC alone. P 2540 was regarded as the optimum anionic flocculant, as its addition

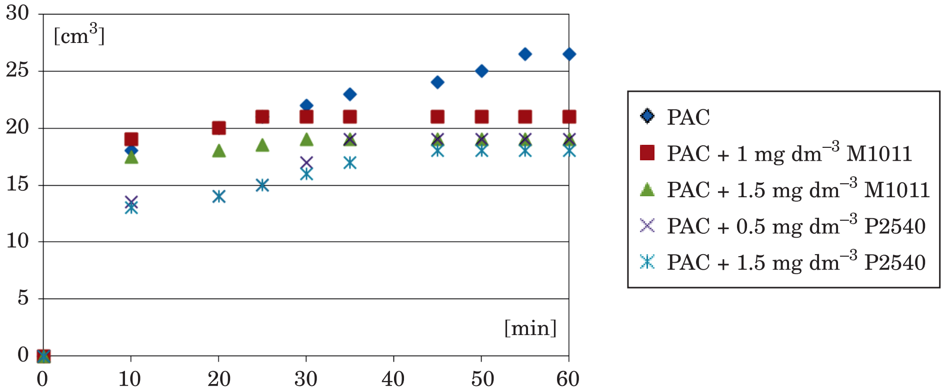

Fig. 2. Characteristics of the sludge sedimentation using PAC and anionic polymers

at 1.5 mg dm^{-3} boosted the effect of PAC by 32%. This was the same as in boosting the effect of PAC with 1 mg dm^{-3} of Z92. A slightly lower effectiveness of the flocculation process was observed when 0.5 mg dm^{-3} of cationic polymer Z92 and anionic polymer M1011 were used. However, the result at 21–23% of reduction in the sludge volume with these flocculants is satisfactory. The values of 32–38% of the sludge volume reduction, achieved with cationic flocculants Z92 and Z63 proved better than 21–32% for anionic flocculants P2540 and M1011. Based on these data, one can claim that better separation of floccules in paper and pulp wastewater can be achieved when cationic organic flocculants Z92 and Z63 are used with an inorganic coagulant.

The enhancing effect of organic polyelectrolytes is additionally enhanced by considerable reduction in the phase separation time. The sedimentation process for cationic flocculants was completed after 30–35 minutes and for anionic flocculants after 30–45 minutes (PAC alone 55 min). It should be stressed that an addition of a small amount of organic flocculants improves the characteristics of phase separation, both in the formation of the minimum amount of sludge and in a considerable reduction of the sedimentation time.

Macromolecular polymers used in the study cause adsorption on colloidal particles to a greater extent than those with small molecules (DAS, SOMASUNDARAN 2004). The authors suggest that such high effectiveness of macromolecular polymers results from the size of their molecules, which ensure high adhesion relative to the surface of adsorption. Therefore, the effectiveness of flocculation can be controlled by adsorption of polymer. Molecules of polymer with a high molecular weight make intermolecular bridging particularly intensive when stable floccules overcome electrostatic interactions. This means that the optimum dose of a macromolecular polymer is relatively smaller than that of a polymer with small molecules (FERRETTI et al. 1997).

The supporting effect of polymers results in an increase in the size and density of floccules during the flocculation phase. Aggregates thus formed improve the effectiveness of phase separation.

Using the macroscopic photographic method allows the size, shape and structure of the aggregates to be determined. In order to optimise the flocculation conditions, measurement of the degree of aggregation and the properties of the aggregates is performed.

The process of flocculation with PAC and the anionic flocculant P2540 resulted in the formation of aggregates with the values of R: 0.02–0.117 mm. Distribution of the number of particles, shown in Figure 3 and Figure 4, provides grounds for determination of the percentage of particles of specific

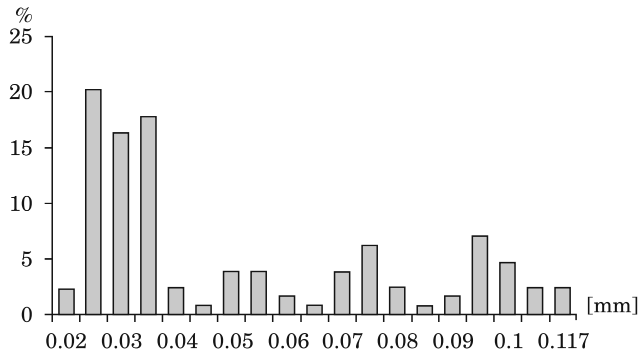

Fig. 3. Distribution of the sizes of aggregates obtained with PAC and P2540

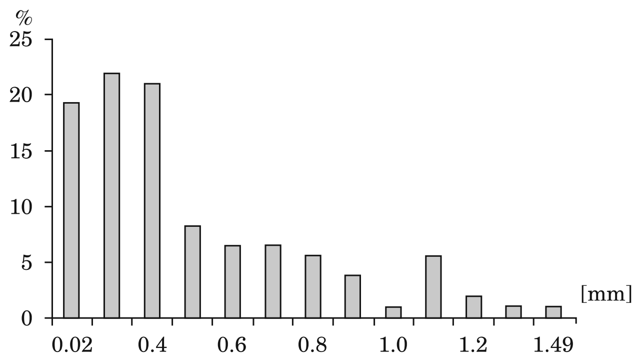

Fig. 4. Distribution of the sizes of aggregates obtained with PAC and Z63

sizes. The distribution of floccules presented in Figure 4 indicates that the highest proportion of floccules had sizes of 0.025–0.035 (53.5% calculate the average value). Floccules with the size of 0.075 and 0.095 mm accounted for approx. 15% of all samples. Figure 4 shows that the size of aggregates formed with the use of the cationic flocculant ranged from 0.02 to 1.49 mm. Such a great difference between the sizes of floccules formed with the anionic and cationic flocculant indicates that the floccules formed with the anionic polymer were less hydrated than those formed with the cationic polymer. Floccules with sizes ranging from 0.02 to 0.4 mm accounted for the largest portion of the size spectrum. The process of aggregation results in the growth of a floccule to a specific limit size, and if it grows further it disintegrates into smaller parts. The sedimentation rate for floccules formed with the anionic flocculant P2540 was equal to 0.12–1.53 mm s^{-1}. The value was higher for aggregates formed with PAC and the cationic – up to approx. 2.5 mm s^{-1} (WIERZBICKA 2000).

Comparison of the sedimentation tests conducted on pulp and paper wastewater with the results of the macroscopic photographic method of aggregates from the suspension $(SiO_2)_n$ reveals the mechanism of action of flocculants of a different ionic character in environments with various chemical features. In pulp and paper wastewater with pH = 5 (the optimum pH value for coagulation), negatively-charged particles (accounting for a majority of impurities) are probably destabilised by polyhydroxy cations "Al_{13}" and cationic flocculants, in accordance with the charge neutralisation mechanism. This is probably the reason for the highest effectiveness of the cationic flocculant Z63 in sedimentation tests and for the minimum volume of the sludge formed underthose conditions. On the other hand, destabilisation of the lattice of positive charge $(SiO_2)_n$ (at pH = 7–8) with "Al_{13}" most probably takes place by bridging with incorporation of the AlO_4^{5-} ion on the micelle surface. In that case, additional support with the anionic flocculant may consist in intensification of the bridging effect. The mechanism of flocculation differs depending on the system pH. This means that at pH = 4.5, neutralisation of the charge may result in the formation of floccules of high density, whereas the density of floccules formed at pH = 7.5 is lower due to neutralisation and intermolecular bridging.

Conclusions

1. The highest effectiveness was achieved with the use of the cationic polymer Z63, which – when used together with PAC – reduced the volume of the sludge by 38% (1 mg dm^{-3}) to 36% (1.5 mg dm^{-3}) as compared to PAC alone.

2. When used with anionic (P2540, M1011) and cationic (Z63, Z92) polymers, PAC considerably reduced the sludge sedimentation time from 60 minutes (PAC alone) to 30–35 min.

3. Aggregates formed in the process of flocculation of silica suspension with PAC and the cationic flocculant Z63 have higher values of R: 0.02–1.49 mm – than those formed with the anionic flocculant P2540 – R: 0.02–0.117 mm.

4. The sedimentation rate of the aggregates formed in the process of flocculation with Z63 v = up to 2.5 mm s^{-1} is higher than with P2540 – 0.12–1.53 mm s^{-1}.

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