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Dual-polymer flocculation with unmodified and ultrasonically conditioned flocculant

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ABSTRACT

Dual-polymer flocculation with unmodified and ultrasonically conditioned flocculant is presented in this paper. In the experiments two types of suspensions, i.e. chalk dust and kaolin clay in RO water were investigated. In the former case the bridging mechanism was expected whereas in the latter case charge neutralization and charge patching mechanisms should be dominant. The measurements were carried out in a laboratory setup for on-line particle size distribution (PSD) analysis consisting of stirred vessel with turbine mixer, laser particle size analyzer Fritsch Analysette 22 and peristaltic pump. The flocculation kinetics is described in terms of PSD and mean particle diameter change in time. Authors proved that ultrasonic conditioning may be an effective alternative for a dual-polymer flocculation where two different flocculants are used. In some cases the mechanical strength of flocs, created by combination of unmodified and conditioned polymers, was improved which resulted in reduction of time needed to achieve the steady state of the system.

1. Introduction

Multicomponent flocculation is a process where at least two aggregating agents are used. According to authors knowledge the first results in field of this topic were reported by Britt [1]. He used a sequential addition of polymers of opposite charge to enhance flocs tenacity in flocculation of pigment filler in a paper stock. Nowadays, some attempts are made to apply this approach in different branches of industry, e.g. mineral processing [2–4] or paper making [5–7]. Moreover, the idea of multicomponent flocculation is extending – different types of components are used.

Multicomponent flocculation is a very complex process. Unlike the single component flocculation, where macromolecules interfere only with the solid surface of particles and with each other, here the system of dependences is a far more complicated. Besides the standard issues concerning interfacial phenomena like the impact of pH or charge densities, adsorption of polymers from ternary polymer – polymer – solvent system is influenced by other factors, like: different affinity of polymeric components to the adsorbent surface, difference in the adsorption of components and dependence on the solvent quality, dependence of adsorption on the presence of another component, solution concentration and the components ratio, molecular mass distribution which is connected to simultaneous proceeding of two processes – competitive adsorbtion of both components and displacement adsorption of one of them, and at last dependence on the ratio of the total adsorbent surface to the solution volume [8]. Furthermore, in case of competitive adsorption from dilute solutions, the time of establishing the adsorption equilibrium is different, being dependent on the polymer pairs [8]. Finally, the structure of adsorption layers is determined by the specific features of this adsorption and by the character of entities adsorbed, e.g. macromolecules and aggregates, separate and common aggregates [8].

At present there are some scientific reports concerning multicomponent flocculation from different points of view. Swerin et al. [5] presented a model of the flocculation efficiency for system of low molecular weight (LMW) cationic polymer, a high molecular weight (HMW) cationic polymer and an anionic particle sol in cellulosic fibre suspension flocculation. The model qualitatively predicted the bridging flocculation behaviour. In experiments a poly(diallyldimethylammonium chloride) (LMW) was used as a side blocking agent. It created a sort of mask forcing more stretched conformation of polyacrylamide (HMW). The montmorillonite particles acted as the additional bonding agents between polymer chains. A similar model for a dual-component system, i.e. cationic poly(acrylamide) and bentonite particles, was developed by Cho et al. [6]. Furthermore, a range of colloidal alumina based inorganic cationic microparticles in a dual-component system was also investigated by Ovenden and Xiao [9]. They observed a synergistic effect between anionic poly(acrylamide) and microparticles which reduced the amount of linear polymer required for effective flocculation.

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In turn, Csempesz and Csáki investigated simultaneous competitive adsorption of uncharged polymers on negatively charged colloidal dispersions and resulting bridging flocculation [10,11]. They proved among others that a synergistic effect may be obtained using polymers blend. It could be due to the formation of an extended conformation of polymers in the mixed adsorption layer as compared to the polymer conformations adopted in the individual adsorption layers. Fan et al. investigated flocculation of alumina particles using sequential addition of non-interacting pair of: polyacrylic acid (PAA) and sodium dodecyl sulfate (SDS) [12], and polyacrilic acid and copolymer of acrylamide and quaternary acrylate salt (Percol) [13]. In Ref. [12] authors demonstrated the impact of the order of polymers addition. When the SDS was added first the conformation of PAA and the suspension stability varied with SDS dosage. Whereas when the PAA was added first, the SDS was masked during adsorption and did not influence neither the PAA conformation nor suspension stability. Authors also indicated that the time of reagentizing had a significant effect on both the adsorption and flocculation. Opposite results using dodecylamine as the cationic surfactant and polyethylene oxide – polypropylene oxide – polyethylene oxide triblock copolymers as the nonionic surfactants were obtained by Şakar-Deliormanli [14]. They achieved a synergistic effect of suspension stability enhancement.

In Ref. [13] authors proposed a mechanism of anchors and tethers. The PAA chains were added as the first to the suspension. They created primary flocs simultaneously becoming the anchors on their surfaces for Percol, which was added as the second polymer and become the tether for the primal flocs. In this way the flocculation can be markedly enhanced by choosing an appropriate pair of oppositely charged polymers. It was also stated that sequential addition is a better mode than co-addition since the polymer adsorption is essentially irreversible. Analogous research extended with the dewaterability analysis was made by Glover et al. [15]. It was shown that dual-polymer systems resulted in low final cake moisture content while still maintaining a reasonably rapid filtration rate. Moreover dual-polymer flocculants of opposite charge gave a lower final cake moisture content when compared to dual-flocculants of like charge.

Lee and Liu [16,17] researched sludge dewatering by dual-polyelectrolytes. They achieved enhanced dewaterability and less chances of overdosing. As in Ref. [12] the order of addition also played an important role. Sludge pre-conditioned with the cationic polyelectrolyte followed with the non-ionic polyelectrolyte exhibited better dewaterability than in reverse order. Cationic chains created more tight primary flocs with negative charged particles. When a non-ionic polyelectrolyte was added, it became adsorbed on the loops and tails of the cationic one by hydrogen bonding and van der Waals forces. In Ref. [17] authors also demonstrated that flocs obtained in dual-polymer flocculation had a much stronger structure than in single polymer conditioning.

An interesting research was done by Yan et al. [18]. They investigated the flocculation efficiency for positively charged alumina particles with a very polydisperse flocculant and compared it with that of a single-component reference polymer. Although no synergistic flocculation effects were found, a wider range for effective flocculation across the optimum dosage point was obtained and larger flocs where created for higher polymer dosages. The role of flocculant molecular weight distribution was also indicated in Ref. [13] where authors stated that a wider distribution can widen the optimum dosage range of the second polymer and is hence preferred.

A different approach to the multicomponent flocculation was presented in Ref. [19,20]. The polymer–surfactant or polyelectrolyte–surfactant complexes (PSC and PEC) were applied in dye removal. PSC as well as PEC nanoparticles bonded disperse dyes due to their size, that is in the same range as the dye molecules, and their structure via hydrophobic as well as electrostatic forces. Another solution of dye removal was proposed by Wei et al. [21]. Authors used a dual system of polyferric chloride and polydimethyldiallylammonium chloride to remove different types of dyes. In some cases a synergistic effect was obtained.

Finally, the application of dual-ionic thermosensitive polymers is worth mentioning here [22]. The usage of oppositely charged polymers led to a creation of complexes adsorbed on the particles surfaces which resulted in lowering the transition temperature dependent on the ratio of dosages of cationic and anionic polymers.

In authors opinion, the biggest disadvantage of multicomponent flocculation is the need of usage of different aggregating agents, e.g. two different polymers. In the result, its application, especially in existing plants, its problematic due to the need of extra storage space or separate mixing tanks and pump systems. It has to be emphasized that polymers have to be aged before application – this time varies from 1 h to even 24 h. At last there is also a possibility that operating staff mix agents by mistake. Therefore we propose a dual-polymer flocculation with unmodified and ultrasonically conditioned flocculant. The idea of ultrasonic conditioning of polymers to enhance dewaterability properties of sludges was presented by Bien et al. [23]. They showed that this type of modification may have a positive impact on the subsequent filtration process. In Ref. [24] the effect of flocculant sonication on the course of flocculation was demonstrated. It was proved that modified polymers gave stronger flocs which resulted in shorter time periods needed to achieve a steady state of the system. Unfortunately, as it should be expected, these flocs were also smaller comparing with the ones received with unmodified polymers. Application of ultrasound in dual-polymer flocculation was presented in Ref. [25]. Authors sonicated a high molecular weight cationic polyacrylamide and used it in polymer blends. However these results were poorly reported.

In most papers quoted above a description of flocculation phenomenon is omitted or weakly presented. There are almost no analysis of the particle size distribution (PSD) of investigated sludge and its change in time. Often, flocculation runs in a small beaker stirred with a magnetic stirrer or in a test cylinder where the mixing is achieved by shaking or rotating. These conditions are far from the real ones existing in industrial scale unit operations. In this paper the course of flocculation process using polymer blends as well as sequential addition of unmodified and sonicated polymers are presented. The results are described in terms of PSD and mean particle diameter time evolution. Proposed solution may be an interesting alternative for dual-polymer flocculation where two different flocculants are used.

2. Experimental

2.1. Materials

In experiments two different types of suspensions were used. The first one was the suspension of commercial chalk dust obtained from Malwa company (Poland) in RO water (Hydrolab Polska, Poland). The second one was the suspension of kaolin clay from LB Minerals (Czech Republic) in RO water. To receive a correct measurement using the laser particle sizer a proper obscuration between 7% and 15% at the beginning and in the end of the flocculation process has to be maintained. For that purpose the concentration of suspensions was set to $\phi = 0.279\ \mathrm{kg/m^3}$ and $\phi = 0.185\ \mathrm{kg/m^3}$ for chalk and kaolin clay, respectively. Appropriate amount of solid matter was weighted in an analytical balance and mixed with small amount of RO water. Such mixture was added to $V = 5.39 \times 10^{-3}\ \mathrm{m^3}$ (full mixing tank) of RO water. Slurry was added while the agitator was working. The pH was measured using digital pH-meter (Elmetron, Poland). It was equal to 8 in case of chalk and