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EFFECTIVENESS OF FLOCCULATION OF MODEL SILICA SUSPENSION BY ORGANIC POLYELECTROLYTES

Elwira Wierzbicka, Barbara Pliszka, Grażyna Ciołkowska-Huszcza

Department of Chemistry
University Warmia and Mazury in Olsztyn

Key words: flocculation, organic polyelectrolytes, turbidity, fractal dimension.

Abstract

Coagulation/flocculation of a suspension of silica SiO_2 was carried out with the use of macromlecular organic polymers which supported the action of two inorganic coagulants – PACl and $Al_2(SO_4)_3$. The results indicate the exceptional effectiveness of cationic and anionic flocculants in coagulation with $Al_2(SO_4)_3$ and an anionic polymer P 2540 in combination with PACl. They also show the correlation between the degree of purification of the liquid phase with 20 mg Al dm^{-3} from $Al_2(SO_4)_3$, supported by flocculants and the fractal dimension D of the aggregates obtained with $Al_2(SO_4)_3$ and organic polymers. An increase in coagulation of the liquid phase corresponds to an increase in the fractal dimension D = 1.52–1.97.

SKUTECZNOŚĆ FLOKULACJI MODELOWEJ ZAWIESINY KRZEMIONKI PROWADZONEJ ZA POMOCĄ POLIELEKTROLITÓW ORGANICZNYCH

Elwira Wierzbicka, Barbara Pliszka, Grażyna Huszcza-Ciołkowska

Katedra Chemii
Uniwersytet Warmińsko-Mazurski w Olsztynie

Słowa kluczowe: flokulacja, polielektrolity organiczne, mętność, rozmiar fraktalny.

Abstract

Proces koagulacji/flokulacji zawiesiny krzemionki SiO_2 prowadzono z zastosowaniem wysokocząsteczkowych polimerów organicznych wspomagających działanie dwóch koagulantów nieorganicznych – PACl i $Al_2(SO_4)_3$. Uzyskane wyniki badań wskazują na szczególną skuteczność

Elwira Wierzbicka, University of Warmia and Mazury, pl. Łódzki 4, 10-957 Olsztyn, Poland, phone: +48 (89) 523 42 47, e-mail: elwiraw@uwm.edu.pl

flokulantów kationowych i anionowych w koagulacji prowadzonej z $Al_2(SO_4)_3$ i anionowym polimerem P 2540 we współpracy z PACl. Dowiedziono, że istnieje korelacja między stopniem oczyszczenia fazy ciekłej za pomocą 20 mg Al dm^{-3} z $Al_2(SO_4)_3$ wspomaganego flokulantami a rozmiarem fraktalnym D agregatów otrzymanych za pomocą $Al_2(SO_4)_3$ i polimerów organicznych. Wzrostowi stopnia skoagulowania fazy ciekłej odpowiada wzrost rozmiaru fraktalnego D = 1.50–1.99.

Introduction

Organic polymers are frequently used in water and wastewater treatment. Water-soluble polymers whose chains contain polar or ionic groups are called polyelectrolytes. Depending on the group's character, they are classed as cationic, anionic or non-ionic. Organic polymers used in water and wastewater treatment can effectively destabilise colloids, but they are usually used in order to support inorganic coagulants.

Literature reports sometimes use the term coagu-flocculation to refer to the process which consists of three consecutive stages: reagent mixing, coagulation and flocculation. Coagulation involves formation of micro-flocs with a size of less than 5 µm, which in the next stage increase in size, forming macro-flocs (< 1 mm) (HANHUI et al. 2004). The addition of organic polyelectrolytes supports the flocculation phase and makes the flocs cluster into larger agglomerates.

Characteristic features of organic polymers include charge density, which is defined as the percentage ratio of ionic groups to all the groups in the chain (BOLTO 1995). When characterising flocculants in terms of their molecular weight and charge density, it is assumed that with a molecular weight of 10^7 the charge density ranges from 50 to 100%; the value for polymers with the molecular weight of 10^8–10^6 is about 25%, and when the molecular weight is about 10^4–10^5 it is about 10%. Both the molecular weight and the charge density play an important role in creating the right conformation of a polymer chain in a solution which, in turn, affects the mechanism of flocculation and sedimentation (BESRA 2004). Emerging new technologies of polymer molecular architecture indicate that highly branched, spatial and interacting polymer conformations are more effective than linear ones and that their action results in more compact and less hydrated flocs (PEARSE 2001). The bridging properties of organic polymers increase the degree of aggregation of colloidal particles, which creates flocs able to sediment. The effectiveness of polymer adsorption depends both on the polymer properties (degree of hydrolysis, spatial structure, ionic strength) and on the characteristics of the systems which are being purified (e.g. the type and size of particles and the available surface and the electrokinetic potential of the dispersed particles and pH of the solution) (GUNGOR and KARAOGLAN 2001).

Research into the phenomenon of aggregation in combination with elements of fractal analysis has led to the development of different models of aggregation (simulation of diffusion-limited aggregation particles DLA, monomer-cluster aggregation, cluster-cluster aggregation controlled diffusion). Being a widely recognised tool, fractal analysis allows users to quantitatively assess the degree of folding or fraying irregular surface of the objects under analysis. When fractal analysis is applied to a description of aggregation, the structure and properties of the post-coagulation sludge can be described in a new, qualitative way (LEE 2002). Characterisation of flocs by this method allows one to determine the compactness of the aggregate structure and the degree of hydration of the sludge (BOTTERO 1989).

The aim of this study was to determine the effect organic polymers on the flocculation effectiveness of a model system of silica suspension with inorganic coagulants of the PACl and $Al_2(SO_4)_3$ type.

Experimental methods

The results of coagulation-flocculation of colloidal solution of silica (SiO_2) at the concentration of 300 mg dm^{-3} are presented. The system turbidity was removed with two aluminium coagulants: PACl and $Al_2(SO_4)_3$ at two levels of dosing. The supporting effect of three macromolecular flocculants has been examined: cationic Z 63, anionic P 2540 and non-ionic PFC 108.

The coagulants contained different amounts of the main ingredients:

– PAC type coagulants contained 47–52 mg Al dm^{-3} and about 97 g Ca^{2+} dm^{-3},

– $Al_2(SO_4)_3$ contained about 9.1% Al.

Chemical coagulation was effected with the standard jar-test procedure:

– fast stirring (400 rpm) – 1min,

– slow stirring (30 rpm) – 15 min,

– sedimentation – 15 min.

Turbidity was determined by the absorption method with a DR 2000 HACH spectrophotometer. Testing organic flocculants was based mainly on the recorded changes in the studied system turbidity. The effectiveness of flocculation was determined from the formula (OZKAN 2003):

$$\text{flocculation effectiveness} = (T_0 - T_f)\ T_0^{-1}$$

where:

T_0 – initial turbidity of the dispersed silica suspension,

T – sample turbidity following the coagulation/flocculation process.

Results and Discussion

The properties of organic polymers were determined with respect to changes in the turbidity of a model system of silica after completing the coagulation/flocculation process. The process was carried out with the use of inorganic coagulants (PACl and $Al_2(SO_4)_3$), both with and without flocculants.

Figure 1 and Figure 2 show the results of examination of the process of coagulation-flocculation of silica suspension with the use of 10 and 20 mg Al dm^{-3} with PACl and three selected organic flocculants with a different ionic character: cationic Z 63, anionic P 2540 and non-ionic PFC 108.

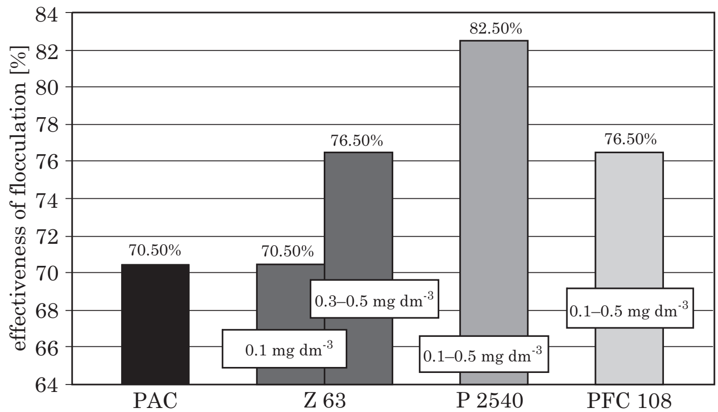

Fig. 1. The effect of the organic polymer dose on the effectiveness of flocculation performed with 10 mgAl dm^{-3} from PACl

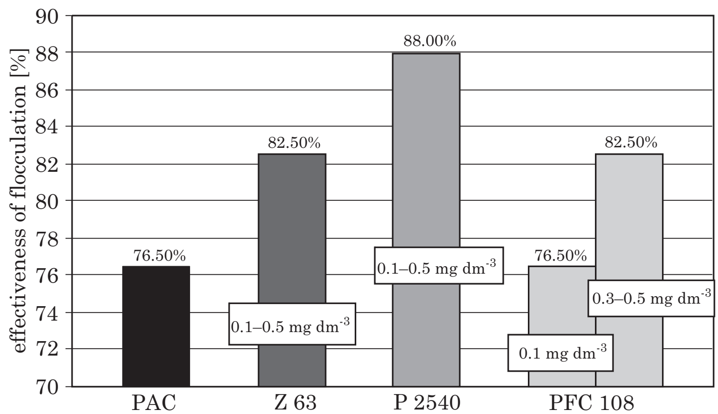

Fig. 2. The effect of the organic polymer dose on the effectiveness of flocculation performed with 20 mg Al dm^{-3} from PACl

The peak effectiveness of flocculation was observed following the use of the lowest dose of 0.1 mg dm^{-3} of the anionic flocculant P 2540 (at both levels of dispensing PACl). Such an amount of the flocculent caused the turbidity to decrease by 82.5% and 88%, respectively. The addition of 10 mg PACl with 0.3 mg of the cationic flocculant Z-63 and 0.1 mg of non-ionic polymer PFC 108 offsets the effect of the double dose of the inorganic coagulant. Anionic flocculants in the model system of silica suspension, used in combination with PACl (10 mg Al dm^{-3}), proved to be more effective in reducing turbidity than the cationic ones. The addition of anionic flocculant can considerably reduce the consumption of the inorganic coagulant. It is probable that the destabilisation of a greater number of positive particles of (SiO_2)n in the presence of anionic flocculants may result in the formation of larger flocs through direct "bridging". This may, in turn, significantly speed up the phase separation.

In general, according to LATTRIGE (1982), the process of destabilisation of electropositive sol of $(SiO_2)_n$ coagulated with PACl runs by bridging $(SiO_2)_n$ micelles with AlO_4^{-5} anions, incorporated in the surface, with "Al_{13}" polycations. It is probable that supporting the process with a cationic flocculant is a result of increasing the number of "bridges" in the system. At the same time, molecules of the anionic flocculant can bridge positive $(SiO_2)_n$. micelles directly, without the need to incorporate negative ions AlO_4^{-5}.

Figure 3 and Figure 4 illustrate the effect of the type and dose of the flocculant on the residual turbidity in the coagulation-flocculation of silica suspension with 10 and 20 mg Al dm^{-3} from another inorganic aluminium coagulant under examination – $Al_2(SO_4)_3$.

Surprisingly good results were achieved when $Al_2(SO_4)_3$ was used in combination with the cationic flocculant Z 63, which completely removed turbidity at a dose as low as 0.3 mg Al dm^{-3}. The data in Figures 1–4 show that

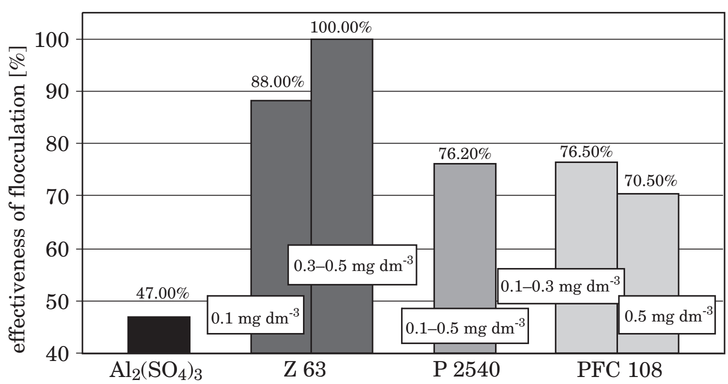

Fig. 3. The effect of the organic polymer dose on the effectiveness of flocculation performed with 10 mgAl from $Al_2(SO_4)_3$

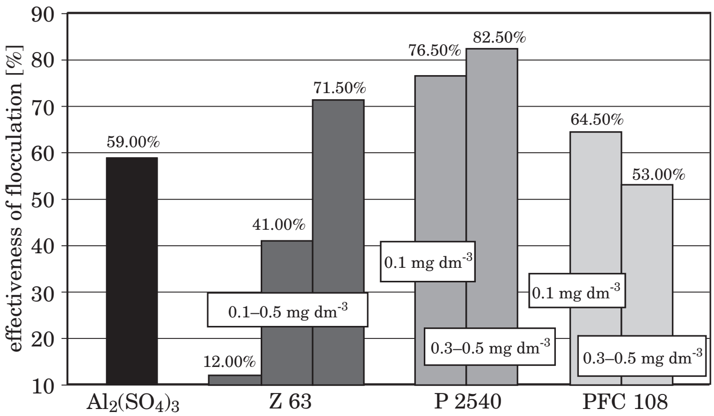

Fig. 4. The effect of the organic polymer dose on the effectiveness of flocculation performed with 20 mgAl dm^{-3} from $Al_2(SO_4)_3$

the effectiveness of the flocculant used in the experiment largely depended on the type and effectiveness of the inorganic coagulant used. Identical doses of 10 mg Al dm^{-3} from PACl and from $Al_2(SO_4)_3$, without any support, gave different effects of coagulation: 70.5% and 47%, respectively. The results confirm the higher coagulative ability of PACl as compared to $Al_2(SO_4)_3$, as suggested by literature reports (BOTTERO et al. 1989). However, it is in the presence of $Al_2(SO_4)_3$ that the process of destabilisation with the cationic flocculant Z 63 proved to be the most effective and resulted in total removal of turbidity in the liquid phase above the sediment after coagulation. This again confirms that an organic flocculant to support an inorganic one should be selected on a case-by-case basis, i.e. for a specific type of wastewater and for a specific type of inorganic coagulant.

Weak effect of the cationic flocculant was observed at 20 mg Al dm^{-3} from $Al_2(SO_4)_3$ (Figure 4). Only the dose of 0.5 mg dm^{-3} Z 63 reduced the turbidity by about 70.5%. Cationic flocculants in the other tests even had a negative effect on the effectiveness of coagulation-flocculation. Such results are difficult to interpret, but some explanation may be sought in the effect of the flocculant, which stabilises the colloidal system of $(SiO_2)_n$, or in some "consumption" of coagulative effect of Al from $Al_2(SO_4)_3$ by the flocculants used in the experiment. The consumption mentioned above could result in the formation of aggregates of the sol particles $\{Al(OH)_3\}_n$ and flocculant molecules. Possible unstable aggregates like {cationic flocculant}-AlO_4^{-5}-$\{SiO_2\}$ can both release $\{SiO_2\}_n$ to the solution (increased turbidity) and restrict access of polycations (Al_{13}) to the surface of $\{SiO_2\}_n$. Due to its size and specific properties (large surface charge), one flocculant particle can disturb the effect of many inorganic coagulant particles (LEu and GOSH 1988). The standard jar test procedure can effectively estimate the effect of organic polymers on the phase separation, expressed as the residue of turbidity liquid above the sludge.

From the point of view of coagulation effectiveness, adequate adjustment of the polyelectrolyte dose is a significant factor. Insufficient contact between the flocculant particles when a dose is too low results in insufficient destabilisation of colloidal particles and poor agglomeration. On the other hand, excessive volumes of polymer cause complete coverage of particles with flocculant, which enables inter-particle bridging and re-stabilisation of the colloidal particles. Optimum flocculation occurs when approximately half of the adsorption sites on the surface of the polyelectrolyte-saturated particles remain free.

The obtained results could be compared to the fraktal analysis of wastewater sludge (SMOCZYŃSKI and WIERZBICKA 2001). The application of a macroscopic photography method allows for determination of the size, shape and properties of the obtained aggregates. Fractal analysis is one of the methods used in structural characterisation of flocs. The fractal dimension D is closely related to the aggregate density. An increase in the object density results in an increase in the fractal dimension D, which makes the aggregates more stable.

The highest values of the fractal dimension D were calculated for the aggregates obtained with $Al_2(SO_4)_3$ and the anionic flocculant P 2540 D = 1.988 and the cationic one Z 63 D = 1.978 (SMOCZYŃSKI and WIERZBICKA 2001). Such high values of D may indicate that aggregates with more compact structure were obtained. BOTTERO and BERSILLON (1989) claim that as the pH of the solution and PACl basicity (R = [OH] : [Al]) increase, the specific available surface Al_{13} decreases. They found that the specific flocs surface, formed as a result of diluting and hydrolysis of polymeric coagulants such as PACl, is significantly larger than that obtained with a monomeric coagulant $Al_2(SO_4)_3$. Moreover, these researchers reported that the degree of contaminant sorption increases with the degree of unfolding of the studied flocs surfaces.

The relatively low values of D = 1.36 (PACl) and D = 1.56 ($Al_2(SO_4)_3$) (SMOCZYŃSKI and WIERZBICKA 2001) for the non-ionic flocculant N 300 may in turn indicate the existence of a loose structure of aggregates and their considerable hydration. The results indicate that there is a clear correlation between the degree of the liquid phase treatment with 20 mg Al dm^{-3} from $Al_2(SO_4)_3$, supported by flocculants, and the fractal dimension D of aggregates obtained with $Al_2(SO_4)_3$ and organic polymers. An increase in the degree of coagulation of the liquid phase (64.5–82.5%) corresponds to an increase in the fractal dimension D = 1.5–1.988 (SMOCZYŃSKI and WIERZBICKA 2001). The values of D_K, D_A and D_N show that the flocculants applied significantly affected the structure and properties of the aggregates. Aggregates bind stronger in the flocculation phase than in coagulation (CHO et al. 2002), which most probably makes the structure of flocs formed by flocculation with an organic polyelectrolyte more stable. Examination of the fractal structures of sludge formed by coagulation and the effect of various factors on the value of their fractal dimension is very important from the practical point of view. Low values of fractal dimensions indicate a low density of aggregates and, in consequence, an increase in the size of voids in the space occupied by it.

Conclusions

1. A positive effect of polyelectrolytes in coagulation using inorganic coagulants was observed in most trials (86%).
2. The highest effectiveness of flocculation (100%) was observed in the case of cationic flocculant Z63 in combination with 10 mg Al dm^{-3} $Al_2(SO_4)_3$. In the other cases, anionic flocculants, acting in combination with PACl (10 and 20 mg Al dm^{-3}) and $Al_2(SO_4)_3$ (20 mg Al dm^{-3}), proved more effective in the model silica suspension.
3. The application of 10 mg PACl with 0.3 mg of the cationic flocculant Z-63 and 0.1 mg non-ionic polymer PFC 108 offsets the effect of the double dose of this coagulant.
4. There is a correlation between the degree of purification of the liquid phase with 20 mg Al dm^{-3} from $Al_2(SO_4)_3$, used in combination with flocculants, and the fractal dimension D of aggregates obtained with $Al_2(SO_4)_3$ and organic polymers. An increase in the degree of coagulation of the liquid phase corresponds to an increase in the fractal dimension D = 1.52–1.97.

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