Polyaluminium silicate chloride—A systematic study for the preparation and application of an efficient coagulant for water or wastewater treatment

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**A B S T R A C T**

The coagulation behaviour of the new coagulant agent polyaluminium silicate chloride (PASiC) was investigated in this study. The main purpose was the examination of several possible derivatives of polyaluminium silicate chloride, based on different basicity (OH/Al molar ratio), silica content (Al/Si molar ratio) and preparation method (co-polymerization or composite polymerization) to evaluate the respective coagulation behaviour of them. Moreover, a systematic study was conducted to define the optimum values of aforementioned major parameters, in order to produce an improved product, in comparison with the commonly applied polyaluminium chloride. Overall, 32 silica-based coagulant samples were prepared with different OH/Al (1–2.5), or Al/Si (5–20) molar ratios and preparation methods. The coagulation performance of PASiC products were evaluated for the treatment of contaminated tap water (in terms of turbidity and of NOM removal, as well as of residual Al concentrations and of zeta-potential measurements). Also, they were examined for the tertiary treatment of municipal wastewater (mainly for phosphates removal). Additionally, the new products were compared with the laboratory prepared PACl, with alum (i.e. Al2(SO4)3·18H2O), as well as with commercially available PACl samples. These experiments were completed with the study of coagulation kinetics by using the Photometric Dispersion Analyzer (PDA), in order to compare the respective floc growth rates. Overall, the obtained results suggest that in order to produce a silica-based polyaluminium coagulant with improved coagulation properties, the basicity (OH/Al ratio) should be between 1.5 and 2.0, the silica content (Al/Si molar ratio) between 10 and 15 and should be prepared preferable with the co-polymerization technique. However, attention has to be given in the specific application of these products, as in the case of tertiary wastewater treatment (phosphates removal) more efficient seem to be the silica-based coagulant with lower basicity (i.e. OH/Al 1–1.5).

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1. Introduction

Several research efforts have been devoted to improve the efficiency of coagulation–flocculation process, a basic and essential treatment technique both for water or wastewater treatment facilities, especially for those handling hazardous or toxic liquid wastes (e.g. tanneries, metal plating, etc.). The tendency was the production of coagulants with improved properties in comparison with the conventional ones, such as aluminium sulfate (alum, Al2(SO4)3·18H2O), or aluminium chloride (AlCl3). After studying the aquatic chemistry and behaviour of simple Al salts, the way for improvement seemed to be their (partial) polymerization, before application. The result of these efforts was the production of a range of pre-polymerized aluminium solutions, referred as polyaluminium chloride (PACl), polyaluminium sulfate (PAS), or polyaluminium chloro-sulfate (PACS), with variable degrees of polymerization. These products and especially the first one (PACl) are used extensively worldwide during the last two decades, with an ever increasing demand. Their properties were intensively examined and have proved to be more efficient in lower dosages and in wider pH, temperature and colloids concentration ranges, than the conventional simpler products, leading to cost and operative more effective treatment [1,2]. Their superiority is related to the different aluminium species distribution in the (pre-)polymerized solutions, as compared with the non-polymerized ones and particularly, is connected with the specific polymer Al13 (Keggin type) [3,4].

In spite of their improved properties, the pre-polymerized coagulants performance still remains inferior, when compared to the performance of organic polyelectrolytes, used, e.g. in
water treatment [5]. In recent years, the relevant research in the coagulation–flocculation field was focused mainly in understanding the behaviour and aquatic chemistry of pre-polymerized reagents, such as polyaluminium chloride, and to the further improvement of their properties. The main reason for the higher efficiency of organic polymers is their higher molecular weight, which implies better flocculation properties. In order to improve the aggregating power of PACI, some efforts have been made during the past few years, regarding the incorporation of silica in its structure. Hasegawa et al. [6] noticed that by introducing metal ions into polymerized silicic acid solution, the molecular weight of the product was increased and the respective stability and coagulation performance were further improved. In this case, the product was rather an inorganic metal-poly-silicate flocculant, where silica was the main component, than a pre-polymerized inorganic coagulant. More recently, research has focused in the incorporation of silica within the pre-polymerized metal solutions, aiming to products with larger molecular weight by the application of two techniques; i.e. either by introducing polymerized silica in the pre-polymerized metal solution, or by introducing polymerized silica in the metal solution, followed by polymerization. The first method is referred as composite polymerization, whereas the latter one as co-polymerization.

The polymerized silica can be obtained from a silicic acid solution, which has the tendency to polymerize by dehydration and to form Si–O–Si anhydride bonds, according to the following general scheme:

\[ n\text{Si(OH)}_4 \rightarrow (\text{OH})_3\text{Si–O–Si(OH)}_3(\text{dimmer}) \rightarrow \text{oligomers} \]

\[ \rightarrow \text{colloidal polymers} \rightarrow (\text{SiO})_n \]

The rate of silicic acid polymerization is strongly pH-dependent, being very fast in neutral and slightly alkaline solutions and extremely slow at the low (acidic) pH values of 2–3 [7]. In order to introduce silica in aluminium solution, the gelation must be avoided and therefore, the maintenance of poly-silicates solution respective pH should be applied around 2, as the method to handle silicates for coagulants preparation. Applying this concept, certain efforts have been made to synthesize and to understand the behaviour and the coagulation efficiency of these coagulants. The coagulation performance particularly, is under extensive investigation during the last few years [5,8–12] in order to evaluate the advantages of new coagulants. However, the coagulation performance of silica-based coagulants was evaluated mainly for the treatment of natural waters and their efficiency has not been examined thoroughly for the treatment of wastewater. Moreover, the evaluation was based mainly on the removal of turbidity and little attention was given to residual Al concentration, or to the removal of (natural) organic matter (NOM). The examination of as many parameters as possible is desirable to get an intergraded approach of coagulation performance, especially regarding the residual aluminium concentration and the removal of NOM [13].

This study aims to complete, intergrades and extent the knowledge obtained by the aforementioned publications. The efficiency and behaviour of several derivatives of silica-based aluminium coagulants was systematically examined, aiming to the production of more generic conclusions. Efforts have been made to define the optimum hydroxyl to aluminium molar ratio and the aluminium to silica molar ratio during their preparation, in order to produce improved coagulants, than the conventional (alum), or simple pre-polymerized (PACl) ones. For this purpose, the coagulation efficiency of all prepared coagulants was tested in contaminated tap water, simulating natural (surface) waters. The coagulants with the more efficient combination of OH/Al and Al/Si molar ratios were further examined and their coagulation performance was compared with the coagulation performance of alum, PACI-18 and laboratory prepared PACI, regarding the impact of pH variation on the treated sample. Furthermore, selected coagulants were applied for the treatment of biologically pre-treated urban wastewater, aiming to the removal of phosphates, as relevant data for the respective coagulants applied for wastewater treatment are rather rarely published in the literature. Additionally, their behaviour and efficiency was compared with simple PACI, or alum coagulants. Finally, the kinetics and dynamics of flocculation ability were studied for the first time for silica-based coagulants by using the Photometric Dispersion Analyzer (PDA), a technique which allows the (relative) comparison of floc’s growth for the tested coagulants during coagulation.

2. Materials and methods

All used chemical reagents were analytically pure chemicals. Deionized water (with conductivity lower than 0.5 µS/cm) was used to prepare all the solutions, except of the solutions used for the synthesis of the coagulants. In this case, deionized water made carbonate free by boiling, was used.

For comparison reasons, commercially available PACI-18 (containing 17.15% Al2O3, with basicity 40% and density 1.365 g cm–3), PACI-14 (containing 14% Al2O3 with basicity 80% and density 1.18 g cm–3), both obtained from Phosphate Fertilizers Industry (Greece), as well as aluminium sulfate (alum, Al2(SO4)3·18H2O, analytical reagent), were also examined.

2.1. Procedure for the preparation of coagulants

2.1.1. Preparation of polysilicic acid solution (pSi)

Water glass solution (containing 10% NaOH and 27% SiO2) was diluted to 0.5 M SiO2 and placed in a plastic beaker. Under magnetic stirring, HCl (1N) was introduced drop wise until the pH reaches 4. The solution was aged for 90 min in pH 4 and then, the pH was decreased to 2, where the solution remained for 60 min before use (containing 0.37–0.38 M SiO2).

2.1.2. Synthesis of silica-based coagulants

The synthesis of coagulants took place at room temperature by the application of two polymerization methods, according mainly to Gao et al. [9], although with certain modifications, i.e. by applying the co-polymerization or the composite polymerization techniques. According to the first procedure, the appropriate amount of pSi was mixed with Al solution and in the mixture was added slowly (under magnetic stirring) the appropriate amount of base solution in order to achieve the desired OH/Al molar ratio. According to the second technique, the base solution was initially added to the Al solution, creating an intermediate PACI solution and then, the appropriate amount of pSi was introduced, in order to achieve the desired Al/Si molar ratio. The respective initial solutions were 0.5 M AlCl3·6H2O, 0.5 M NaOH (as the added base) and the aforementioned polysilicic acid solution. The base addition rate (achieved by a peristaltic pump) was 0.1 ml/min and the stirring speed was 700–800 rpm. The final volumes of the obtained solutions samples were about 40–65 ml and the final aluminium concentration was fixed for all coagulants at 0.13 M.

The total number of the newly prepared modified alternative coagulants was 32, with the OH/Al molar ratios 1, 1.5, 2, and 2.5 and the Al/Si molar ratios 5, 10, 15, or 20. Polyaluminium chloride solutions were also prepared (PACLab) for comparison reasons under the same conditions, but without the addition of silicates. The coagulants prepared with the co-polymerization technique are referred as PASiC, whereas the coagulants prepared with the composite polymerization technique are referred as PACSi.
to the basicity and to the Al/Si molar ratio, the coagulants are referred as follows: PASiC with OH/Al = 2 and Al/Si = 10 as PASiC2/10, while PACi with OH/Al = 2 as PACi2. Please note also that basicity = [(OH/Al)/3] × 100 [2]. For PACi-18 the basicity is 40, therefore the OH/Al ratio is 1.2, i.e. relatively low, as compared to OH/Al ratio 2 for the case, e.g. of PACi2.

2.2. Coagulation performance

The zeta-potential was measured by using a Laser Zee Meter 501, the pH by using a Metrohm Herisau pH-meter and the turbidity measurements were performed by a HACH RATIO/XR Turbidimeter. The absorbance at 254 nm, as a convenient indicator of natural organic matter presence, was measured with a Schimadzu UV/vis spectrophotometer, by using a 1 cm path length quartz cuvette.

2.2.1. Jar-tests using contaminated tap water (simulating surface water)

For the determination of coagulation efficiency of the prepared coagulants and their comparison with the performance of conventional ones, a jar-test apparatus (Aqualytic) with six paddles was used. The treated sample (1 L) was made of tap water, clay (kaolin) suspension (commercially available) and humic acids (Aldrich). The initial concentration of clay suspended particles was 10 mg/L, and that of humic acids 5 mg/L. Table 1 displays the specific properties of the initial water sample. As flocculant aid a common anionic polyacrylamide (Magnaflock LT25, Ciba SC LTD, commercially available) was used in concentrations equal to the 1/10th of the respective concentration of inorganic coagulants. The jar-test experimental conditions (based upon preliminary relevant experience) are presented in Table 2. Shortly (within 1 min) after the addition of the coagulant (i.e. during the initial rapid mixing stage) 30 ml of sample was withdrawn for zeta-potential measurements. The flocculant aid was introduced just 15 s before the initialization of slow mixing period. At the end of these experiments about 50 ml of sample was withdrawn 5 cm below the liquid surface for further analytical determinations. The concentrations of coagulants are expressed as mg Al/L in the case of PACi and alum, and as mg (Al + Si)/L in the case of PASiC and PACSi. The experiments were repeated two to three times and the average values are shown in the figures; usually, the variance between the obtained separately values were within 3–5%.

pH adjustment (when needed) was accomplished by the addition of the proper amount of 2N HCl or NaOH solutions in the sample under stirring.

2.2.2. Jar-tests with biologically pre-treated wastewater

The prepared coagulants were also applied for the tertiary treatment of biologically pre-treated municipal wastewater, to evaluate their coagulation efficiency mainly by means of phosphates removal. Table 1 displays the specific properties of the initial waste water sample. The coagulation experiments were conducted in 500 ml samples and the applied jar-test experimental conditions are shown in Table 2. The conditions were slightly different from the respective in the aforementioned experiments (i.e. those related to contaminated tap water treatment), as resulted after preliminary experiments.

2.2.3. Residual aluminium concentration

The residual aluminium concentrations were determined with the eriochrome cyanine R standard method [14]. In dilute and buffered to pH 6 solutions, aluminium complexes with eriochrome cyanine R dye and results to a colored compound, which absorbs light with maximum at 535 nm.

2.2.4. Determination of phosphates concentration

The concentration of phosphates was determined with the ascorbic acid standard method, according to APHA [14].

2.2.5. Study of coagulation kinetics

The extent of aggregation was also examined and the flocculation dynamics was accomplished by using a continuous flow optical flocculation monitor (PDA 2000, Rank Brothers, UK). Fig. 1 displays a schematic diagram of the experimental set-up, operated in non-recycling mode. The test suspension of 1.5 L tap water, containing 5 mg/L of clay and 5 mg/L of humic acids, was placed in a 2 L beaker and stirred with the paddle of a jar-test apparatus. The suspension flows through the measuring transparent plastic cell (having 3 mm diameter), where it was illuminated by a narrow light beam (of 850 nm wavelength), with the help of a peristaltic pump. The pump was placed after the PDA apparatus for preventing the eventual floc breakage, eventually caused by the mechanical forces of the pump. The applied flow rate was 30 ml/min in order to have laminar conditions in the transfer tube, hence avoiding flocs breakage.

All experiments were conducted at room temperature, without the addition of flocculant aid, to prevent the excessive growth of flocs and the blockage of connecting tubing (diameter 3 mm).

The PDA measures the average transmitted light intensity (dc value) and the root mean square (rms value) of the fluctuating component. The ratio (rms/dc), or flocculation index (FI) provides a sensitive measure for the aggregation of particles. The FI value is strongly correlated with the respective floc size and always increases as flocs grow larger, providing a useful (although relative) indication of floc growth, eventually breakage and re-growth, which allows comparisons to be made between the different coagulants and under different shear conditions and coagulant concentrations [15,16].

3. Results and discussion

3.1. Comparison of prepared coagulants

The main purpose of this study was to evaluate the optimum characteristics of silica-based coagulants, by means of different polymerization degrees (employing different OH/Al molar ratios), silica content and preparation method, in order to achieve improved products, when compared to the conventional coagulants, such as alum, or pre-polymerized (without the presence of silica) coagulants, i.e. polyaluminium chloride. Considering the aforementioned properties of new coagulation reagents, it is worth noting that the polymerization degree is mainly related with the % content of medium size Al polymers (mainly Al12), whereas the increase of OH/Al molar ratio generally results to the increment of this content, as well as of the polymerization degree.
The first step in this effort was the preliminary application of all prepared coagulant samples, aiming to obtain an initial approach about their coagulation behaviour and to define the relatively most efficient between them. For this purpose, coagulation experiments were conducted with the synthetic clay–humics (model) sample. The initial concentration of coagulants in this case was 2 mg/L and the measurements included the determination of residual turbidity, the measurement of UV absorbance at 254 nm, as well as the residual aluminium concentration.

In the case of coagulants prepared with the co-polymerization technique (denoted as PASiC, Fig. 2), it seems that their behaviour is quite different, in accordance with the obtained polymerization degree and the silica content. It is clear that the relatively worst results are due to the higher silica content, i.e. Al/Si 5 (for a given OH/Al value), except of the residual aluminium parameter (but only in the case of PASiC with OH/Al ratio 1.5). Regarding the residual Al concentration, an important issue from the public health point of few, which is also connected with the overall performance of coagulation, it seems that the detrimental effect of higher silica content is less significant (particularly for OH/Al ratio 1.5–2.5). The aluminosilicates formation probably leads to molecules of larger size, which can be removed easily through coagulation and sedimentation. Observing the impact of OH/Al ratio on the coagulation performance, it can be seen that the least effective OH/Al ratio is 1. Based on the evaluation of best performance, e.g. the lowest residual turbidity, the UV absorbance at 254 nm and the residual aluminium concentration, it seems that the more suitable OH/Al molar ratio should be 2.0. Specifically, the overall lowest residual turbidity, as well as lowest residual aluminium concentration, was achieved by using the sample PASiC 2/10.

The coagulants with the highest silica content are also the less effective in the case of reagents prepared with the composite polymerization technique (PACSi, Fig. 3), with some exceptions, regarding the residual aluminium concentration. Worth noting is that with OH/Al ratio 2.5, all coagulants exhibit almost the same performance, regarding the residual aluminium concentration. It is obvious that the hydrolytic reactions taking place and the respective products of them can differ accordingly to the applied preparation technique. In composite polymerization the higher polymerization degree (achieved by OH/Al 2.5 ratio) [17], lead to similar behaviour of coagulants, independently of silica content. The most efficient coagulant regarding turbidity removal seems to be the PACSi with OH/Al ratio 1.5 and Al/Si ratio 10, whereas regarding the residual Al concentration, seems to be the PACSi with OH/Al ratio 2 and Al/Si ratio 15. Regarding the UV absorbance removal, the PACSi with OH/Al 1.5 ratio and Al/Si ratio 15 was found to be the most efficient reagent.

It is obvious that the examined different preparation parameters can influence significantly the properties of silica-based coagulants. Considering the polymerization degree, a medium or high OH/Al ratio should be desirable, e.g. 1.5–2.5. However, during the aforementioned experiments it was noticed that the coagulants with OH/Al ratio 2.5 were quite unstable, as compared to the others. Within 30 days after preparation, formation of precipitate was observed and sudden increase in the stored coagulants turbidity was recorded. The increase of turbidity was more intense in the coagulants prepared with the co-polymerization technique and those containing higher silica content. Based on these observations and on the coagulation performance, the more suitable OH/Al molar ratio should be 1.5–2.0. The impacts of applied preparation technique and of the Al/Si molar ratio on the coagulation performance were further examined.

### 3.2. Impact of Al/Si ratio and of preparation technique on coagulation performance

Jar-tests were conducted in order to evaluate the impact of silica content and of specific preparation technique, i.e. co-polymerization or composite polymerization, on the coagulation efficiency of obtained reagents. The selected coagulants, based on the previous results, were PASiC or PACSi with OH/Al 2.0. The experimental conditions were described in the previous Section 2.2.1 and the applied coagulant doses were equal to 1, 2, or 3 mg (Al + Si)/L.

In Figs. 4 and 5 the results of turbidity and UV\textsubscript{254} nm absorbance reduction, relatively to the Al/Si ratio and to the coagulant dosage, have been presented.

In the case of PASiC (Fig. 4a, turbidity removal) it is clear that the most efficient Al/Si molar ratio is 10, especially when applying lower coagulant dosages. At the concentration of 2 mg (Al + Si)/L, the performance of PASiC products with Al/Si ratio 15 converge to that of PASiC with Al/Si ratio 10, while when applying even greater dosages the differences between the efficiency of examined coagulants become rather smaller, except of the coagulant with the greatest silica content (Al/Si ratio 5). The latter sample seems to be the least efficient for all the examined concentrations. Almost the same observations can be made, regarding the reduction of UV\textsubscript{254} nm absorbance (Fig. 4b). PASiC with Al/Si ratio 10 seems to be the most efficient and PASiC with Al/Si ratio 5 seems to be the least efficient. The difference in this case is that PASiC with Al/Si ratio 20 exhibits equal or better performance than PASiC with Al/Si ratio 15. For the PACSi products, Al/Si ratio seems to have about the same impact on coagulation performance (Fig. 5), whereas the PACSi samples with Al/Si ratios 10 and 15, which present almost the same coagulation behaviour, regarding turbidity and UV absorbance reduction. Again, the least effective Al/Si molar ratio is 5.

Fig. 6 illustrates the turbidity and UV absorbance removal rate (%) with the use of silica-based coagulants. It seems that the preparation method does not present any major effect on the respective coagulation performance. In the case of Al/Si ratios 5, 10 and 20,
PASiC seems to exhibit a slightly better performance than PACSi and only in the case of Al/Si ratio 15 the PACSi seems to act slightly better to PASiC. Generally, the coagulants prepared with co-polymerization, show better coagulation performance.

Based upon these results, it is suggested that a silica-based coagulant with improved properties should have medium to high basicity (i.e. OH/Al molar ratio 1.5–2.0), medium silica content (i.e. Al/Si molar ratio 10–15) and should be prepared preferable by the co-polymerization technique. In general, the obtained results are in good agreement with the relevant observations of Gao et al. [5,9,10].

However, Cheng et al. [11] concluded also that OH/Al ratio should be between 1.5 and 2, but regarding silica content, the more suitable Al/Si ratio should be 5.

3.3. Impact of pH value on the coagulation performance

PASiC 2/10 and PACSi 2/10 samples were selected for the further examination of pH influence on their performance. Additionally, they were compared with the performance of laboratory prepared PACi2, which presents relatively higher degree of polymerization [17], as well as with the commercially available product PACi–18 (presenting lower degree of polymerization), and with alum (i.e. the respective non-polymerized coagulant). The pH values were varied between 6 and 9, the dosage of examined coagulants was 2 mg/L.
and the rest experimental conditions were remained the same, as in the previous Section 2.2.1. Fig. 7 demonstrates the coagulation behaviour of these coagulants with respect to pH. The removal of turbidity and of UV absorbance at 254 nm, the residual aluminium concentration and the zeta-potential values of the suspensions after the addition of examined coagulants are also presented.

It can be seen that the less effective coagulant, regarding pH values greater than 6, is alum. All pre-polymerized coagulants behave better in a wider pH range, especially in the alkaline one, which relies on the respective mechanisms of coagulation. By the dissolution of any aluminium salt, various hydrolysis reactions immediately occur and several primary products can are formed [3,4,18]. In the case of non-polymerized, or with very low degree of polymerization coagulants, the coagulation efficiency is based mainly on the Al(OH)₃ precipitate formation, than on the charge neutralization mechanism, which is favoured in pH values 6.5–7 [19]. In the more alkaline region, Al(OH)₄⁻ formation begins and with increasing pH it becomes dominant, resulting in the dramatic drop of coagulation efficiency.

This fact is also obvious, considering the residual Al concentration (Fig. 7c), where alum and PACl-18 exhibit the relatively worst performance. This is possibly due to the fact that in the case of PACl₂lab and silica-based coagulants, the higher degree of pre-polymerization results in lower monomeric Al³⁺ concentration and in the presence of medium and larger size Al polymers [17], which are more resistant to further hydrolysis. In this case it can be suggested that the coagulation behaviour is at certain degree “controlled” and it is not any longer depended upon the Al(OH)₃ precipitate formation. The relevant mechanisms rely more upon the charge neutralization mechanism, as well as to bridging and adsorption interactions between the colloids to be removed and the Al polymers.

However, at the pH value 6 the behaviour of coagulants is different. Regarding turbidity and UV absorbance removal, PACl-18 and alum seem to be more effective. From the zeta-potential measurements (Fig. 7d), it can be observed that at this pH value a charge reversal occurs in all cases, possibly leading to the re-stabilization of colloids. The bigger the polymerization degree of the coagulant, the greater the positive zeta-potential of resulting colloids is, although leading eventually to re-stabilization phenomena. Nevertheless, the residual aluminium concentration is again higher for the case of alum, as shown in Fig. 7c. Considering the fact that the hydrolysis of Al³⁺ is retarded in pH 6 and that in this pH value the Al(OH)₃ specie exists mainly in dissolved form, the significance of pre-polymerized aluminium species is obvious, and especially in the case of silica-based coagulants, because they found to be the most effective.

The pre-polymerized coagulants exhibit similar performance, regarding the removal of turbidity. Slightly better seem to be the laboratory PACl2 and the PASiC samples. Regarding the reduction of UV absorbance at 254 nm, the respective differences are easier to be
distinguished, i.e. PASiC and PACI present again better performance, with little differences between them. The relevant advantage in the use of the silica-based coagulants can be concluded from the lower residual aluminium concentration (Fig. 7c). The differences are quite large, when compared to the coagulants with none or lower polymerization degree, such as alum or PACI-18. PASiC and PACSi seem to create significantly less residual aluminium concentration, especially at the higher (alkaline) pH region, whereas alum and PACI-18 seem to be less appropriate for use, due to the respective higher residual aluminium concentration. In the pH range 7–9, i.e. the usual pH range of natural waters, the residual aluminium concentration remains under (or close to) 200 μg/L, which is the EU maximum permissible concentration limit for drinking water ([20]). Considering that this concentration refers to total aluminium and not only to the dissolved fraction, the superiority of silica-based coagulants is obvious. Moreover, PASiC and PACSi seem to behave even better than the laboratory prepared PACI, although the later is presenting higher polymerization degree, and between them PASiC seems to be slightly better than the PACSi reagent. It is noted that the addition of silicates into PACI with certain OH/Al molar ratio can result in the decrement of medium Al polymers content; therefore, PACI has greater polymerization degree, than the PASiC or PACSi samples, although with the same OH/Al molar ratio [17]. The formation of aluminosilicate complexes seems to play a significant role, probably because the presence of silica enhances the resistance of aluminium species for further hydrolysis.

Generally, the change of pH seems to have little effect on the coagulation performance of PASiC and PACSi. The optimum pH range of alum is around the pH 7 and that of PACI-18 around the pH 7–8. Laboratory prepared PACI2 (with relatively higher polymerization degree) is effective in the pH range 6.5–8.5, whereas for silica based coagulants and especially for PASiC the optimum pH range can be even broaden to pH values 6.5–9.

In Fig. 7d the change of zeta-potential values with respect to the pH values of test suspensions after the application of coagulants is presented. In all examined coagulants a similar pattern was observed, i.e. rather lower (more negative) values were observed at the pH around 9, where the charge neutralization is less effective, whereas an increase of zeta-potential values was noticed (hence becoming less negative) towards the more acidic pH values. In all the examined cases at pH around 6 a charge reversal was observed. Clearly, the greatest effect on surface charge exhibits the coagulant with the highest polymerization degree, i.e. PACI2 [17], and it can be supposed that it presents also the greatest charge neutralization capacity. The least effective products were alum and PACI-18. PASiC and PACSi show moderate effect, with similar behaviour. The incorporation of silica reduces the charge neutralization capability of coagulants, a negative effect which seems to be compensated by the increase of colloids/particle size of these coagulants, as observed also in literatures [8,9]. Additionally, observing that the PACI, PASiC and PACSi samples at pH around 7 show zeta-potential measurements of created colloids/particles closer to zero and hence, approaching the charge neutralization mechanism, the better performance of them in circum-neutral pH value is understandable. The better performance of silica-based coagulants with the variation of pH values was also observed by other researchers [5,8,9,11], although it was not described with details.

It should be mentioned that after the addition of aluminium coagulants in the conducted coagulation experiments, a decrease in the pH values of the samples was observed (data not shown), especially in the case of alum. The acidic character of Al3+ cation and its hydrolysis products (possessing higher positive charge) are responsible for this decrease. The pre-polymerized coagulants contain already a percentage of these resistant to further hydrolysis species and show a lower (i.e. less significant) effect to the pH value of samples. As the basicity, or the OH/Al molar ratio further increases, this impact is less noticeable. In the case of silica-based coagulants, the incorporation of silica chains into the structure of PACI results in a decrement of coagulants charge density, as shown by the respective zeta-potential measurements. Furthermore, the possible conjunction of aluminium species with silica bridges enhances the resistance of them to hydrolysis. As a consequence, the silica-based coagulants have shown a weaker influence on the pH values of samples, than the simple pre-polymerized coagulants.

3.4. Phosphates removal

Regarding the phosphates removal efficiency, all PASiC samples with molar ratio Al/Si 10 were tested and compared to the commercially available PACI-18, PACI-14 and alum coagulants. The aqueous sample to be treated was biologically pre-treated urban wastewater, collected from the exit of a full-scale wastewater treatment plant (Thessaloniki, N. Greece). The main characteristics were: initial concentration of inorganic phosphates 10.1 mg/L (measured as ortho-phosphates), turbidity 13.5 NTU, UV absorbance (at 254 nm) 0.181 and pH 8.

All tested coagulants were found to be efficient for the removal of turbidity (i.e. residual turbidity was below 0.15 NTU for all cases—data not shown). However, their efficiency was not equally good, regarding the removal of natural organic matter, although their behaviour was similar, except that of PASiC1/10 sample, which showed better performance (data not shown). Fig. 8a illustrates the results of phosphates removal for initial coagulant concentrations 10–50 mg/L. It can be seen that the less effective coagulant was...
PACl-14 (having basicity 80%, which corresponds to OH/Al ratio 2.4 and relatively high degree of polymerization), whereas the most effective were PACl-18 (having basicity 40%, corresponding to OH/Al ratio 1.2 and relatively low degree of polymerization [17]), as well as alum and PASiC samples with OH/Al 1 and 1.5. With the latter coagulants the dose needed for limiting the concentration of phosphates under 1 mg/L (according to the respective legislation limit for ecologically sensitive areas) is about 20–30 mg/L, whereas with the rest coagulants the respective concentration (dose) needed is more than 40 mg/L. In Fig. 8b the percentage of phosphates removal, regarding the OH/Al ratio in the PASiC samples, is presented.

It can be noted that the removal efficiency increases as the ratio OH/Al decreases, corresponding also to the decrease of polymerization degree [17], unlike the aforementioned results obtained with the contaminated tap water samples and that the most efficient reagent in this case was PASiC with the least OH/Al molar ratio (i.e. OH/Al = 1). The relevant explanation relies in the respective mechanism of phosphate removal through the addition of coagulants. Jiang and Graham [21] reported that the removal of phosphates by the application of coagulation/flocculation process involves the following two major mechanisms: (a) the interaction of phosphates with the soluble aluminium forms (chemical complexation), or with the non-soluble (charge neutralization) complexes, producing compounds with generic formulae $\text{Al(OH)}_3 - x\text{PO}_4$, which can either adsorb onto the positively charged Al(III) hydrolysis species, or may act as cores for the precipitation of Al(III) hydrolysis products. (b) The direct adsorption of phosphates onto aluminium hydrolysis products, mainly referred to precipitation with insoluble $\text{Al(OH)}_3$ (sweep flocculation). Additionally, Ratnaweera et al. [22] suggest that with the lower basicity coagulants (i.e. those with low OH/Al ratio) the dominant mechanism is the co-precipitation with $\text{Al(OH)}_3$ (sweep flocculation), while with the high basicity coagulants (i.e. those with high OH/Al ratio) the dominant mechanism is the formation of Al–PO$_4$ complexes.

Based upon the obtained experimental results and the aforementioned possible mechanisms, it is suggested that the dominant mechanism during phosphates removal is sweep flocculation, as the most efficient coagulant was the PASiC with the inferior basicity. This suggestion is also supported by considering the pH values of the aqueous sample to be treated, as for the pH values higher than 7, the formation of $\text{Al(OH)}_3$ is favoured. Also, in this pH region the most dominant phosphate species are $\text{H}_2\text{PO}_4^-$ and $\text{HPO}_4^{2-}$, and the latter is assumed to have higher affinity for the $\text{Al(OH)}_3$ floc at higher pH values. Boisvert et al. [12] studied the
phosphates adsorption, by using alum and polyaluminium-silicate-sulfate (PASS) samples. They concluded that the presence of silicate at low level (i.e. Al/Si ratio 25) does not present any notable effect on phosphates adsorption. The same conclusion, regarding the efficiency of phosphates removal, can be also deduced from this study, as the performance of the best PASiC sample with the higher level of silicates' content (i.e. Al/Si ratio 10) was almost equal to the performance of alum and PACl-18. According to our knowledge, very little information was published so far, regarding the coagulation performance of the new silica-based coagulants, when applied in the tertiary wastewater treatment for the removal of phosphates.

### 3.5. Kinetics of coagulation

The monitoring of coagulation–flocculation kinetics by the Photometric Dispersion Analyzer may provide useful information, considering the extent of aggregation and the flocculation dynamics. The overall process can be divided into two separate procedures, which are taking place subsequently, i.e. the coagulation (destabilization of the colloids), which takes place shortly and immediately after the addition of (inorganic) coagulant, and the flocculation, where the previously destabilized particles aggregate to form larger flocs (usually after the appropriate addition of organic polyelectrolytes). During the initial coagulation stage (rapid mixing period), the FI or ratio \((R)\) remains in low values (lag phase) and begins to increase suddenly, when the subsequent flocculation stage (slow mixing period) takes place. As flocculation proceeds, the ratio increases up to a maximum value and finally, equilibrium between the formation and the breakage of flocs occurs, where the ratio values remain relatively constant. The final plateau of \(R\)-values shows the obtained degree of particle aggregation [23–25].

Selected PDA experiments were conducted in order to compare the extent of aggregation and consequently, the floc size generated with the application of PASiC 2/10, PACSi 2/10 (the relatively more efficient silica-based coagulant samples in surface water treatment), alum, PACl-18 and laboratory prepared PACl. Fig. 9a displays the floc growth of contaminated tap water suspension, containing 5 mg/L clay and 5 mg/L humic acids (initial turbidity 9.9 NTU, UV absorbance at 254 nm 0.116, pH 7.6). The initial 120 s represent the fast mixing period (velocity of mixing paddle at 160 rpm, or 200 s\(^{-1}\) expressed as velocity gradient units), where the destabilization of colloids occurs and the floc growth is not remarkable. The aggregation begins during the subsequent slow mixing period (at 45 rpm) and the respective ratio values increase.

The shorter duration of lag phase is desirable in water treatment, due to energy and time savings. From Fig. 9a it is clear that the lag phase lasts longer for the PACl-18 sample and much longer for the alum addition. In the case of all laboratory prepared coagulants the lag phase was significantly shortened, with similar patterns for the three examined coagulants. Moreover, a significant difference between the coagulants behaviour can be observed regarding the rate of ratio increment until it reaches its maximum values. This rate is higher for PASiC and PACSi compared to the other coagulants, indicating quicker flocs growth after the lag phase for the silica-based ones. Finally, the extent of flocculation seems to differ significantly between all examined coagulants, and specifically it can be observed that with silica-based coagulants (particularly with PASiC) the ratio takes higher values, when compared with all the other PACI samples. The floc size decreases with the decrease of the basicity of aluminium coagulants without the presence of silica, whereas alum seems to exhibit the worst performance. As a result, it can be suggested that the silica addition in PACI coagulants results in a more rapid progress of particle aggregation and bigger floc size increment, enhancing flocculation and sedimentation in water treatment processes.

Furthermore, the impact of velocity gradient in floc growth was studied for the selected cases of PASiC2/10 and PACl2 samples. Fig. 9b illustrates the ratio variation with time for the velocity gradient values 200 s\(^{-1}\) (160 rpm), 241 s\(^{-1}\) (180 rpm) and 282 s\(^{-1}\) (200 rpm) and for the PASiC reagent. It seems that the increase of fast mixing intensity has not any noticeable effect for the lag phase duration, but affects negatively the floc growth of the silica-based coagulants. Increasing shear stress results in floc breakage, unlike the case of PACI. As it can be noticed from Fig. 9c, when PACI is used, the increase of velocity gradient has variable effects. A minor increase (180 rpm) results in a small decrease of lag phase duration and a significant increase of floc size. By increasing further the mixing rate, floc breakage occurs and the floc size decreases. The fact that the floc breakage occurs for the case of PASiC addition, when a lower mixing rate was applied (241 s\(^{-1}\)), shows again that the formed flocs are of greater size, indicating that the incorporation of silica chains results in the increment of molecular weight of coagulants components. In the case of PACI the size of hydrolyzed species is smaller, the flocs formed are also smaller and this allows...
the application of higher mixing rates to obtain improved floc size. However, despite the increase of floc size with the application of higher gradient values for the case of PACl, still the respective ratio remains lower, than for the case of PASiC.

4. Conclusions

Several silica-based polyaluminium chloride derivatives were systematically examined, leading to the following optimized conditions for their preparation, according to the respective coagulation performance data: OH/Al ratio 1.5–2, Al/Si ratio 10–15, whereas as preparation technique the co-polymerization should be pre-

ferred. As a result, the final selected product (referred as PASiC*) exhibits better coagulation performance for the treatment of contaminated natural waters, than the conventional coagulants (e.g. alum), or the pre-polymerized commercial coagulants (PACl-18), or even the laboratory prepared PACl, which presents comparatively higher polymerization degree. The great advantage in the use of PASiC* seems to be the lower level of residual aluminium concentration, which remains in the treated water sample. The control of residual Al is necessary, due to the respective legislation limits (EU < 200 µg Al/L, USA < 50 µg Al/L) and it can be problematic, when conventional coagulants are being used. Moreover, the superior performance of PASiC* has proved to be more resistant in pH variation, than PACl, as it has been shown that PASiC* is effective over a pH range of 6.5–9, i.e. the usual pH range of natural waters, where PACl even that with the higher polymerization degree, seems to be less sufficient above the pH 8.0. Finally, considering the results from the kinetics of coagulation it is clear that with the silica-based coagulants bigger flocs are formed, indicating that the incorporation of polymerized silica can result to the enhancement of floc size and growth.

However, the results obtained from the treatment of simulated natural water seem not to be directly and equally applicable to the tertiary wastewater treatment, aiming to the removal of phosphates. It was shown that the efficiency in this case was reversely related to the polymerization degree and more efficient among the silica-based coagulants proved to be the PASiC sample with the lowest OH/Al molar ratio (equal to 1). The nature and the composition of treated aqueous sample, as well as the respective treatment purposes are the major factors, which designate the performance of a coagulant and its ability for a specific application. When compared to PACl and alum, the performance of most efficient PASiC sample did not substantially differ, regarding the removal of phosphates.

Acknowledgements

Thanks are due to the Greek Ministry of Development (General Secretariat for Research and Technology) which supported this research through the PENED program (25%) and to the European Union, which co-founded this program (75%). This research is part of the Ph.D. Thesis of N.D. Tzoupanos.

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