

COAGULATION-FLOCCULATION PROCESSES IN WATER/WASTEWATER TREATMENT: THE APPLICATION OF NEW GENERATION OF CHEMICAL REAGENTS

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Abstract: The aim of this paper is to provide an overall description of coagulation-flocculation process and its applications in water and wastewater treatment. The significance of coagulation – flocculation in the area of water and wastewater treatment is reviewed and evaluated, emphasizing on the series of applications employed, including destabilization of colloids, removal of inorganic and organic matter (particulate and/or dissolved), removal of metals and anions (arsenic, phosphate etc), as well as removal of pathogen microorganisms. Furthermore, the latest developments in the coagulation field, regarding the evolution of the coagulation reagents, are also under investigation. The development of simple pre-polymerized coagulants (i.e. polyaluminium chloride,) seems no longer to be sufficient enough. The need for more effective coagulants has lead to the development of new coagulant categories, via the introduction of various additives in the structure of pre-polymerized coagulants. The first effort was reported 15 years ago, suggesting the use of silica in the form of polysilicates for such a purpose. Nowadays, the range of additives has expanded, including organic compounds, such as anionic, cationic or non-ionic polyelectrolytes, leading to new composite coagulants. Overall, it is evident that the tendency in the coagulation field nowadays is the production of modified composite coagulants, which they are becoming more and more complicated, regarding their composition, but also more effective, when compared with the traditionally applied reagents.

Key-Words: Coagulation; flocculation; composite coagulants; inorganic additives; organic additives.

1. Introduction

The need for drinking water of high quality is increasing, as the non-polluted water sources are continuously decreasing. Additionally, the discharge criteria of wastewaters are becoming stricter, according to the new legislation in force, in order to prevent environmental pollution and/or infection of drinking water sources. It is evident that more effective water and wastewater treatments are needed.

A very important step in water and in wastewater treatment is the coagulation-flocculation process, which is widely used, due to its simplicity and cost-effectiveness. Regardless of the nature of the treated sample (e.g. various types of water or wastewater) and the overall applied treatment scheme, coagulation-flocculation is usually included, either as pre-, or as post-treatment step. The efficiency of coagulation-flocculation strongly affects the overall treatment performance; hence, the increase of the efficiency of coagulation

stage seems to be a key factor for the improvement of the overall treatment efficiency.

The whole treatment process of coagulation – flocculation can be divided into two distinct procedures, which should be applied consecutively. The first one termed coagulation, is the process whereby destabilization of a given colloidal suspension or solution is taking place. The function of coagulation is to overcome the factors that promote the stability of a given system. It is achieved with the use of appropriate chemicals, usually aluminium or iron salts, the so-called coagulant agents. The second sub-process, termed flocculation, refers to the induction of destabilized particles in order to come together, to make contact and thereby, to form large agglomerates, which can be separated easier usually through gravity settling [1]. Coagulation usually completes in a very short period of time (e.g. about 10 s), whereas flocculation occurs usually over a period of 20 to 45 min. It is a common practice, especially in Greece, the enhancement of particles aggregation

Table 1. Classification of particle sizes [1].

Particle size (mm)	Classification	Examples	Total surface area (m ² /cm ³)	Time required to settle 100 mm, if specific gravity = 2.65
10	Coarse dispersion (visible to naked eye)	Gravel, coarse sand, mineral substances, precipitated and flocculated particles, silt, macroplankton	6×10^{-4}	0.1 s
1			6×10^{-3}	1 s
10^{-1}			6×10^{-2}	13 s
10^{-2}	Fine particulate dispersion (visible under microscope)	Mineral substances, precipitated and flocculated particles, silt, bacteria, plankton, and other organisms	0.6	11 min
10^{-3}			6	20 hours
10^{-4}			60	80 days
10^{-5}			600	2 years
10^{-6}	Colloidal dispersion (submicroscopic)	Mineral substances, hydrolysis and precipitated products, macromolecules, biopolymers, viruses	6000	20 years
$<10^{-6}$	Solution	Inorganic simple and complex ions, molecules and polymeric species, polyelectrolytes, organic molecules, undissociated solutes		

during the 2nd step by the addition of organic polyelectrolytes, the so-called flocculant aids, or simply flocculants.

2. Coagulation – flocculation in water and wastewater treatment

The suspended material in waters and in wastewaters mostly arise from land erosion, the dissolution of minerals, the decay of vegetation and from several domestic and industrial waste discharges. For a given water or wastewater, such material may comprise suspended, dissolved organic and/or inorganic matter, as well as several biological organisms, such as bacteria, algae or viruses. This material has to be removed, as it causes deterioration of water quality by reducing the clarity (e.g. causing turbidity or colour), causing infection, and eventually carrying toxic compounds, adsorbed on their surfaces. In addition, organic matter is the main precursor to the formation of disinfection by-products, when chlorine is applied as disinfection agent.

Table 1 [1] classifies according to the size the common materials present in waters or wastewaters. Particles smaller than around 10^{-5} mm may be referred as colloids and particles smaller than 10^{-6} mm as solutions. It can be noticed that with decreasing size, the time required for settling increases, up to several years for certain solutions ingredients. Due to the very small size, the only way for settling and the subsequent separation is to come closer, to make contacts and to form larger particles, which can be settle easier. This procedure however, is hindered due to the homonymous negative charge this material carries. The

electrostatic repulsive forces constrain the particles from approaching each other and the suspension is characterized as stable; therefore, long time period is required for settling.

In order to accelerate the settling time, destabilization is required, denoting the importance of coagulation. The destabilization can be achieved with one, or a combination of two or more of the following mechanisms, after the addition of a coagulant agent [2, 3]:

- 1) Compression of the electrical double layer.
- 2) Adsorption and charge neutralization.
- 3) Adsorption and interparticle bridging.
- 4) Enmeshment in precipitate (by using of excess coagulant dose, “sweep flocculation”).

After the destabilization, flocculation promotes the aggregation and flocs formation, usually after the addition of an appropriate flocculant agent. Two general types of flocculation can be identified: micro-flocculation (or perikinetic flocculation), in which particles aggregation is brought about by the thermal motion of fluid molecules (Brownian motion) and macro-flocculation (orthokinetic flocculation), in which particle aggregation is brought about by inducing velocity gradients and mixing in the suspension [3].

Coagulation-flocculation is used widely during water or wastewater treatment. It is an integral treatment step in the surface or underground waters treatment, intended for human consumption. Typical applications are the removal/separation of colloids and suspended particles, of natural organic matter, or of metal ions. In wastewater treatment, additional applications include the removal of toxic metals, anions (i.e. phosphates), color, odor etc.

3. Coagulation reagents

3.1 Metal coagulants

The commonly used metal coagulants fall into two general categories: those based on aluminium and those based on iron. This paper deals with the aluminium based coagulants, hence these will be described further.

The most widely used metal coagulant is probably the aluminium sulfate ("alum"), which has been used for water treatment during the past decades. It is commonly manufactured from the reaction of bauxite ores with sulfuric acid. Evaporation of water in the process results in a dry product, having the approximate formula $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{-}18\text{H}_2\text{O}$, and with an Al content ranging from 7.4 to 9.5%. It is supplied as powder or in liquid form and its applications include water or wastewater treatment.

A product prepared from alum and sulfuric acid is acidified aluminium sulfate (acid alum). It is supplied as a liquid and is used mainly in paper-making industry. Other Al coagulants are the aluminium chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) and the sodium aluminate (NaAlO_2). The first one is supplied as liquid (containing 10.5% Al) and is used widely for sludge conditioning. The latter is usually supplied as a viscous, strongly alkaline and corrosive liquid (containing 13% Al). It is rarely used alone, but generally with alum to obtain some specific results, i.e. in the treatment of highly colored waters [1, 3].

The application of simple metal coagulants (conventional) is widespread, especially due to the relatively low cost and the simpler application route. However, they exhibit several disadvantages, such as the need for pH adjustment before or after treatment, the sensitivity to temperature changes, the need for higher dosages because the charge neutralization is not usually sufficient, the sensitivity to sample specific characteristics and composition, as well as the excessive sludge production.

3.2 Pre-polymerized coagulants

Several research efforts have been devoted to improve the efficiency of coagulation-flocculation process. After studying the aquatic chemistry and the behavior of simple Al salts, the way for improvement seemed to be their (partial) polymerization. The result of these efforts was the production of a range of pre-polymerized aluminium solutions, referred as polyaluminium chlorides (PACl), polyaluminium sulfates (PAS),

or polyaluminium chloro-sulfates (PACS), with variable degrees of polymerization. These products and especially the first one (PACl) are used extensively worldwide during the last decades, with an ever increasing demand. Their properties were intensively examined and have proved to be more efficient in lower dosages, in wider pH, temperature and colloids concentration ranges, than the conventional simpler ones, leading to cost and operative more effective treatment [3, 4].

Their superiority is related to the different aluminium species distribution in the polymerized, as compared with the non-polymerized solutions. Aluminium exists in water solutions and at pH values < 3 as six-coordinated Al^{3+} ion. With increase of pH value, the aluminium ion begins to hydrolyze, and various products can be formed. The hydrolyzation of Al ion is extremely complicated, involving hydrolysis and polymerization reactions, thus leading apart from various monomeric, also to several polymeric species formation [5]. With conventional coagulants, these reactions are entirely uncontrolled, and the coagulation efficiency is based more to $\text{Al}(\text{OH})_3$ formation (around the pH 6.5-7) and less to charge neutralization, as the hydrolysis reactions are proceeding fast and hence, the concentration of positively charged Al ions is restricted. In the case of PACl, the pre-polymerization aims to control up to a certain extent the aforementioned reactions.

With the partial neutralization of Al solution by adding a base solution and then by aging, these reactions may take place at some extent and various Al species can be formed. The most important reaction is supposed to be that leading to $\text{Al}(\text{OH})_4^-$ formation. This aluminium anionic form is claimed to be the precursor for the polymeric Al_{13} creation [6]. $\text{Al}_{13} (\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{6+,7+})$ with ϵ -Keggin structure is one of many possible PACl polymeric compounds, like dimmers (e.g. $\text{Al}_2(\text{OH})_2^{4+}$), trimers (e.g. $\text{Al}_3(\text{OH})_4^{5+}$) among several others, even larger than Al_{13} i.e. with more than 13 aluminium atoms (e.g. $\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{24}^{18+}$), which transform continuously from one form to another [7]. However, Al_{13} is claimed to be the most stable aluminium specie in a partially neutralized aluminium solution [8] and the improved coagulation properties of PACl are thought to be due to its existence, i.e. increased charge neutralization capability (coagulation) and increased molecular size and aggregation ability (flocculation). Further on, the decrease of monomeric Al in favor of Al_{13} and of the other

polymeric compounds eliminates the hydrolysis reactions and therefore, results in a minor impact of pH value after treatment.

The production of pre-polymerized coagulants involves the partial neutralization of an Al solution with a base solution. Many parameters can affect the properties of the final product, i.e. the base addition rate, the stirring speed, the synthesis temperature, the presence of other anions (e.g. Cl^- , SO_4^- , CO_3^{2-}), the aging time etc. The most important parameter however, is claimed to be the molar ratio of bound hydroxide to the concentration of metal cations (i.e. the OH/Al molar ratio). It is referred as basicity and is also used to describe conveniently the polymerization degree of coagulant agents.

4. New generation coagulation reagents

In spite of their improved properties, the pre-polymerized coagulants performance still remains inferior, when compared to the performance of organic polyelectrolytes, e.g. when used in water treatment [9]. In recent years, the relevant research in the coagulation-flocculation field has focused mainly in understanding the behaviour and aquatic chemistry of pre-polymerized coagulants, 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 (MW), which implies better flocculation properties. Thus, the increase of molecular weight and size of the pre-polymerized coagulants is thought to be the way for further improvement.

The general concept followed is, the introduction of various additives in the structure of a pre-polymerized coagulant, in order to produce a homogenous, stable product with higher MW and improved coagulation-flocculation performance, than the initial reagent. The challenge to confront is the desirable combination of higher efficiency and cost-effectiveness, which are the basic prerequisites for the development of new products. Various additives were examined, which can be classified into two main categories; inorganic and organic. These compounds and the respective products derived, based on aluminium coagulants, will be described in the following.

4.1 Inorganic additives

A suitable additive for the improvement of flocculation properties is thought to be polymerized

silica. Hasegawa et al. [10] noticed that by introducing metal ions into polymerized silicic acid solution, the molecular weight of the product increased and the respective stability and coagulation performance were improved. In this case, the product was rather an inorganic metal-polysilicate 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.

Polymerized silica can be obtained when the concentration of monosilicic acid ($\text{Si}(\text{OH})_4$) in aqueous solution exceeds the solubility limit of amorphous silica, or otherwise by bringing the solution temporarily into the pH-concentration range of oversaturation with respect to amorphous silica [11, 12]. Excess monomers in the solution gradually disappear to form polymers. The polymers, or polysilicic acid, consist of silica tetrahedrons that are linked via silicon-oxygen-silicon bonds (e.g. $\equiv\text{Si}-\text{OH} + \text{HO}-\text{Si}\equiv \rightarrow \equiv\text{Si}-\text{O}-\text{Si}\equiv + \text{H}_2\text{O}$) [12]. Various species can be formed, e.g. $\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$, $\text{Si}_3\text{O}_5(\text{OH})_5^{3-}$ etc., and exact nature and the extent of their formation is affected by the temperature, the concentration of silica, the presence of other ions, the pH value and the aging time. Soluble, internally hydrated, polymeric silicic acids of colloidal dimensions, or discrete particles of colloidal size, can be present. The most important parameter that affects the kinetics of silica polymerization is the pH value. Particularly, the polymerization is thought to be catalyzed by hydroxyl anions and is very fast at neutral or slightly alkaline pH range. Over pH value 9, the reaction rate decreases. Furthermore, by aging the polymerization can lead to the formation of bigger aggregates and finally, to gel formation (amorphous $(\text{SiO})_n$). In order to avoid gelation and to preserve the polysilicates at soluble form, the solution has to be brought outside the insolubility range. This can be achieved by acidifying the solution to pH values 2–3. Particularly, at pH around 2 the polymerization rate is retarded enough and the polysilicates are stable in soluble form for several days [11-13].

Based on these observations and the use of a suitable silicic acid source, i.e. the sodium silicate solution or water glass, several efforts have been made for the introduction of acidified polysilicates into the structure of pre-polymerized coagulants. The mixed product in the case of aluminium is called polyaluminium silicate chloride, though it should be rather referred as a category of coagulation reagents, because with different combinations of OH/Al or Al/Si molar ratios, various reagents can be produced. Polyaluminium silicate chloride has shown superior coagulation performance, than the conventional or simple pre-polymerized coagulants in water or wastewater treatment [9, 14, 15]. The better performance can be attributed to the alteration in a specific degree of the coagulants composition. Specifically, it has been proved that the introduction of silica chains into the structure of PACl increases the molecular weight of the coagulants components with the formation of alumino-silicate complexes, thus leading in enhanced aggregating power and bigger-denser flocs formation [9, 14-17].

4.2 Organic additives

Organic polyelectrolytes are typical hydrophilic colloids and contain certain functional groups, which may be ionizable. When these groups dissociate, the polymer molecules become charged, either positively or negatively, and are thus referred to as cationic or anionic polyelectrolytes, respectively. If no ionizable groups are present, the polymers are termed as non-ionic [1].

They can be classified according to their origin into two main categories, the natural and or synthetic polymers. Natural polymers (biopolymers) have long been used as flocculants (bioflocculants). Typical examples are starch derivatives that are pregelatinized and water-soluble. These can be starches, anionic oxidized starches, or amine-treated cationic starches. Other classes include polysaccharides, such as guar gums, tannins, chitosan and the alginates [3, 18].

Although natural polyelectrolytes have the advantage of being toxic-free, the use of synthetic polyelectrolytes is more widespread. They are in general more effective as flocculants, principally due to the possibility of controlling properties, such as the number and type of charged units and the molecular weight. Moreover, they are much cheaper, than those made from natural sources.

Synthetic organic polymers are made either by homo-polymerization of the monomer, or by co-polymerization of two monomers. Polymer

synthesis can be manipulated to produce polymers of varying size (MW), charge groups, number of charge groups per polymer chain (charge density) and varying structure (linear or branched). Many synthetic polyelectrolytes are based on polyacrylamide and its copolymers with polyacrylic acid. Typical examples are the hydrolyzed polyacrylamides (anionic, MW 10^4 - 10^7 g/mole), polydiallyldimethyl ammonium chloride (poly-DADMAC, cationic, MW 10^4 - 10^7 g/mole) and various polyacrylamides (nonionic, MW 10^5 - 10^7 g/mole) [18].

Organic polymers are not generally used as primary coagulants. Only in certain cases cationic polyelectrolytes will be applied for the destabilization of colloids (coagulation) and usually, in conjunction with inorganic metal salts. The primary use of polymers is as flocculant aids, whereas non-ionic or anionic polyelectrolytes are added after the addition of an inorganic coagulant [19]. Despite their efficiency, their use is accompanied with significant drawbacks, such as the increased treatment cost. Considering that apart from the product cost itself, which is higher than inorganic salts, polymers are delivered usually in solid form and hence, a separate dissolution set-up is needed, which further increases the treatment cost. Furthermore, the existence of remaining unreacted monomers results in residual toxicity in the treated sample.

The combination of an inorganic salt (coagulant) and a suitable polyelectrolyte (flocculant) into one reagent is thought to improve, apart from the treatment efficiency of the inorganic salt, the overall cost-effectiveness. No addition of a flocculant aid will be needed any more, whereas the introduction of the polyelectrolyte into the structure of the metal salt will also significantly reduce the eventual residual toxicity.

These suggestions lead to the production of modified inorganic coagulants with organic additives, a field that is under investigation nowadays. All the aforementioned charged or not charged polyelectrolytes can be used for this purpose, with different impact in the nature of the new product. Particularly, by the introduction of a cationic polyelectrolyte into the structure of a pre-polymerized metal coagulant, the charge neutralization capability is mainly expected to be improved, and in a lower extent, the aggregating effect as well. Moreover, the usage of an anionic polyelectrolyte with higher molecular weight (as compared to cationic) would further improve the aggregating ability. In this case, however, the anionic polymer should have weaker anionic

charge, in order not to deteriorate extensively the charge neutralization strength of the combined coagulant agent. A non-ionic polyelectrolyte would have a minor effect in the coagulants charge density (possible negative), but would increase significantly the flocculation ability. Key factors affecting strongly the properties of the combined, modified coagulant are the charge, MW and content of the polyelectrolyte.

Some efforts have been reported, regarding the combination of PACl with various anionic, cationic and non ionic organic polymers [20] and the combination of PACl with poly-DADMAC [21, 22]. Although the research in this field is in an initial stage, promising results were obtained from the aforementioned, publications regarding the coagulation performance.

The introduction of the polyelectrolyte can be accomplished by two procedures, as in the case of silica addition, i.e. with the co-polymerization, or the composite polymerization. The content of the polyelectrolyte (PE) in the final product is usually expressed as the Al/PE ratio (mg/L), can take values between 5 and 20 and together with the aforementioned parameters in the case of pre-polymerized coagulants, designates the properties of the final product.

4.3 Applications of the new generation coagulants

In the 3rd IASME/WSEAS Conference (Crete, 2007) [23], the authors presented the superior performance of polyaluminium silicate chloride, as compared to the performance of conventional or simple pre-polymerized coagulants in water treatment. Particularly, it was shown that the incorporation of polymerized silica enhances the aggregation ability, as the duration of flocs growth period decreases and the size of generated flocs increases. This enhancement compensates efficiently the decrease in coagulants charge neutralization capability due to silica addition, as the coagulation performance of PASiC was clearly better, especially regarding residual Al concentration. The advantages of PASiC in water treatment can be summarized in the more efficient treatment, using lower dosages of coagulants and in a wider pH range, whereas the Al concentration that remains in the treated sample is significantly lower.

A matter that has not been considered yet in detail is the application of polyaluminium silicate chloride in wastewater treatment. Table 2 demonstrates the results of the post-treatment of

biologically pre-treated landfill leachates with coagulation-flocculation [24]. This kind of wastewater is difficult to be further treated, mainly due to its bio-refractory organic content (humic substances). The performance of PASiC (OH/Al = 1, Al/Si = 15) is evaluated and compared with the respective performance of a conventional coagulant (alum, OH/Al = 0), as well as with two simple pre-polymerized coagulants, a widely used commercial product with slightly higher polymerization degree (PACl-18, OH/Al = 1.2) and a laboratory prepared PACl solution with the same polymerization degree (PACl_{lab}, OH/Al = 1). Turbidity, UV absorbance at 254 nm (corresponding to the presence of Natural Organic Matter / NOM) and chemical oxygen demand (COD) were among the monitored parameters during these experiments.

From table 1 it can be seen that the least effective coagulant in almost all cases is alum, whereas the most effective is PASiC. The highest removal efficiencies for all the examined parameters are achieved with the new composite coagulant for the highest dosage added (300 mg/L). Worthnoting is the fact that with the addition of alum or PACl_{lab} over 200 mg L⁻¹ the quality of treated sample was deteriorated by means of turbidity (denoted as 0% removal). Therefore, the further increase of concentration leads to overdosing, reversibility of coagulation phenomena and re-stabilization of colloids. However, in the case of silica-based coagulants, the addition of even 300 mg L⁻¹ results in the further improvement of treated wastewater (leachate) characteristics, thus with these coagulants the application of higher dosages is possible in order to obtain better treatment results.

Nevertheless, it should be mentioned that in order to prepare a superior novel silica-based coagulation reagent, specific attention has to be given to the polymerization degree, the silica content, as well as to the preparation method, because from these experiments it was revealed that composite coagulants with different OH/Al and Al/Si molar ratios or preparation methods can be most efficient in different cases [14, 24]. As an example, fig. 1 displays the percent (%) removals of organic matter (by measuring the UV absorbance at 254 nm), after treating a synthetic wastewater sample (simulated domestic wastewater) with several polyaluminium silicates coagulants, containing different silica content (Al/Si 5-15, Al/Si=0 corresponds to PACl). It can be noticed that not all composite coagulants are more efficient than PACl, but only those with Al/Si = 10 or 15.

Regarding the new composite coagulants with organic additives, the evaluation of their **Table 2.** Comparison of coagulation* performance for several Al-based coagulants when applied in waste water treatment.

Coagulant	Turbidity removal (%)			Absorbance at 254 nm removal (%)			COD removal (%)		
	Coagulant dosage (mg/L)			Coagulant dosage (mg/L)			Coagulant dosage (mg/L)		
	50	100	300	50	100	300	50	100	300
Alum	65	72	0	16	29	39	30	51	61
PACI-18	83	88	77	18	31	70	31	46	73
PACI _{lab}	84	88	0	20	32	71	35	49	63
PASiC	86	90	94	19	33	74	32	51	77

* Initial turbidity 4.5 NTU, initial absorbance at 254nm 2.740, pH of treated sample 8.6

Table 3. Comparison of coagulation* performance for polymers-based coagulants, when applied in water treatment.

Coagulant	Turbidity removal (%)			Absorbance at 254 nm removal (%)			Residual Al concentration (mg/L)		
	Coagulant dosage (mg/L)			Coagulant dosage (mg/L)			Coagulant dosage (mg/L)		
	2	4	6	2	4	6	2	4	6
PACI _{lab}	94	97	97	70	73	79	150	172	178
PACPE	95	99	99	83	86	87	155	150	158

* Initial turbidity 16.2 NTU, initial absorbance at 254nm 0.120, pH of treated sample 7.78

coagulation performance in water treatment has started recently.

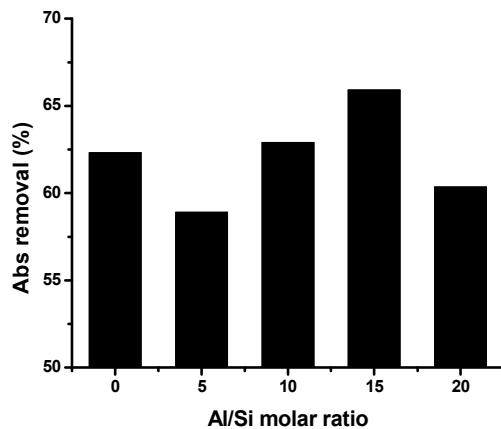


Fig. 1. Absorbance removal after treating a synthetic wastewater sample with PACI and several polyaluminium silicate chlorides reagents. Concentration of coagulants 50 mg/L, initial absorbance at 254 nm 1.38, pH 7.45.

Table 3 illustrates the comparative results of kaolin-humic acid model suspension (simulated surface water) treatment with laboratory prepared PACI (OH/Al= 2) and a composite coagulant prepared with the incorporation of a non-ionic polyacrylamide (Magnaflock LT-20) in PACI (OH/Al = 2). This specific polymer is used in water treatment facilities in Greece, whereas the respective Al/Si ratio (mg/L) in the final product (PACPE) was 15. The coagulation experiments were conducted with the use of the same PE as

flocculant aid in the case of PACI (in concentrations equal to 1/10 of PACI concentrations), whereas in the case of PACPE no flocculant aid was added. Both examined coagulants are efficient in turbidity removal. Significant differences can be observed in absorbance removal, where PACPE exhibits better performance. It can be noticed that even with relatively low dosage of coagulants (2 mg/L), the absorbance removal is over 80% with PACPE, whereas with PACI the respective removal is 70%.

Moreover, the residual Al concentration is much lower in the case of PACPE, especially for the dosages of 4 and 6 mg/L. The most important advantage however, is related with the amount of PE used in both cases. Particularly, it was noticed that with 30% less PE, the performance of PACPE was better than the respective performance of PACI. Not only the two treatment steps (coagulation-flocculation) were combined in one, but better treatment was achieved with lower amounts of polyelectrolyte, pointing out not only the superior coagulation performance, but also the cost effectiveness related with the use of the new composite coagulation agents.

The improved properties of the composite coagulants with polyelectrolytes can be devoted to the better flocculation properties, compared to the conventional coagulants, similarly with the case of PASiC. Figure 2 illustrates the results of the examination of coagulation kinetics for the aforementioned in the coagulation experiments pre-polymerized and composite coagulants. The flocs growth (presented as Ratio values), relatively to

time (sec) is presented. Two distinct effects can be noticed, due to PE addition in the PACI reagent. The first is related with the time needed for the flocs to growth, the so-called lag phase. It is evident, that in the case of the composite coagulant the lag phase is significantly limited. The latter is related with the extent of flocs growth, and specifically with the respective maximum Ratio values achieved with the two coagulants. Higher Ratio values indicate greater flocs size [25], therefore it can be concluded that with the composite coagulant bigger flocs are formed.

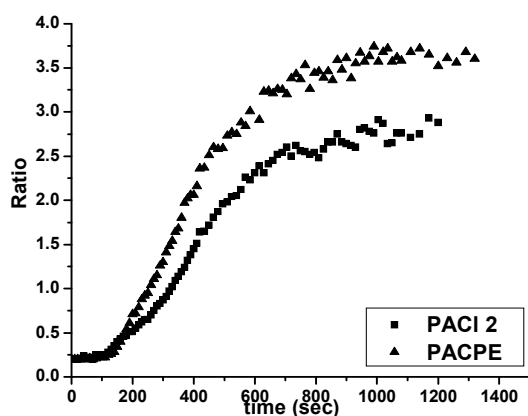


Figure 2. Kinetics of coagulation of the Al-based coagulants.

5. Conclusions

The application of the new generation of coagulation reagents exhibits several advantages, compared to the conventional and simple pre-polymerized coagulants. The incorporation of various additives, inorganic or organic, results in an increment of molecular weight and components size, which compensates efficiently the decrease of charge neutralization capability in the new coagulants. Overall they present better treatment performance, lower residual metal concentration and wider effective pH range, which are the main advantages of the composite coagulants. In the case of composite coagulants with polyelectrolytes, the economical benefits should also be taken into consideration.

However, despite the aforementioned advantages of newly prepared coagulants, the research in the coagulation-flocculation field is continuing. Optimization of the preparation conditions is needed, especially in the case of composite coagulants with organic additives, and

determination of the specific properties that imply superior coagulation performance. Coagulants with different basicities and/or additives content may have different applications (water/wastewater treatment). Moreover, suggestions for the preparation of new reagents appear in the literature continually, i.e. different combinations of Al and Fe in one reagent and possible addition in a second step of an inorganic or organic compound.

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References:

- [1] Bratby, J. (ed), Coagulants, in *Coagulation and Flocculation in Water and Wastewater Treatment*, second ed., IWA Publishing, London, 2006, pp. 50-68.
- [2] Duan, J., Gregory, J., Coagulation by hydrolysing metal salts, *Advances in Colloid & Interface Science*, Vol. 100-102, 2003, pp. 475-502.
- [3] J.C. Crittenden, R.R. Trussel, D.W. Hand, K.J. Howe, G. Tchobanoglous (eds), Coagulation, mixing and flocculation, in: *Water Treatment: Principles and Design*, second ed., John Wiley & Sons, New Jersey, 2005, pp. 643-779.
- [4] S. Sinha, Y. Yoon, G. Amy, J. Yoon, Determining the effectiveness of conventional and alternative coagulants through effective characterization schemes, *Chemosphere*, Vol. 57, 2004, pp. 1115-1122.
- [5] Z. Jia, F. He, Z. Liu, Synthesis of polyaluminium chloride with a membrane reactor: operating parameter effects and reaction pathways, *Industrial and Engineering Chemistry Research*, Vol. 43, 2004, pp. 12-17.
- [6] Parker, D.R. and Bertsch, P.M., Formation of the 'Al₁₃' tridecameric polycation under diverse synthesis conditions, *Environmental Science & Technology*, Vol. 26, 2002, pp. 914-921.
- [7] Bi, S., Wang, C., Cao, Q. and Zhang, C., Studies on the mechanism of hydrolysis and polymerization of aluminium salts in aqueous solution: correlations between the Core-links model

and Cage-like keggin- Al_{13} model, *Coordination Chemistry Reviews*, Vol. 248, 2004, pp. 441-455.

[8] Wang, M. and Muhammed, M., Novel synthesis of Al_{13} -cluster based alumina materials, *NanoStructured Materials*, Vol. 11, 1999, pp. 1219-1229.

[9] Gao, B.Y., Hahn, H.H., Hoffmann, E., Evaluation of aluminum-silicate polymer composite as a coagulant for water treatment, *Water Research*, Vol. 36, 2002, pp. 3573-3581.

[10] Hasegawa, T., Hashimoto, K., Onitsuka, T., Goto, K., Tambo, N., Characteristics of metal-polysilicate coagulants, *Water Science & Technology*, Vol. 23, 1990, pp. 1713-1722.

[11] Chan, S.H., A review on solubility and polymerization of silica, *Geothermics*, Vol. 18, 1989, pp. 49-56.

[12] Stumm, W., Huper, H., Champlin, L., Formation of polysilicates as determined by coagulation effects, *Environmental Science & Technology*, Vol. 1, 1967, pp. 221-227.

[13] Dietzel, M., Dissolution of silicates and the stability of polysilicic acid, *Geochimica et Cosmochimica Acta*, Vol. 64, 2000, pp. 3275-3281.

[14] Zouboulis A.I. and Tzoupanos, N.D., Polyaluminium Silicate Chloride – a systematic study for the preparation and application of an efficient coagulant for water or wastewater treatment, *Journal of Hazardous Materials*, 2008, in press.

[15] Cheng, P.C., Chi, F.G., Yu, R.F., Shi, P.Z., Evaluating the coagulants of polyaluminium silicate chlorides on turbidity removal, *Separation Science & Technology*, Vol. 41, 2005, pp. 297-309.

[16] B.Y. Gao, Q.Y. Yue, B.J. Wang, The chemical species distribution and transformation of polyaluminium silicate chloride coagulant, *Chemosphere*, Vol. 46, 2002, pp. 809-813.

[17] Song, Y.H., Luan, Z.K., Tang, H.X., Preparation and characterisation of polyaluminium silicate chloride coagulant, *Environmental Technology*, Vol. 24, 2003, pp. 319-327.

[18] Bache, D.B. and Gregory, R. (eds) *Flocs in Water Treatment*, IWA Publishing, 2007, London, UK.

[19] Kim, Y.H. (ed.), *Coagulants and Flocculants; Theory and Practice*, Tall Oaks Publishing, 1995, Littleton, USA.

[20] Tang, H., Shi, B., The characteristics of composite flocculants synthesized with inorganic polyaluminum and organic polymers, in Hahn, H., Hoffmann, E., Odegaard, H. (eds) *Chemical Water and Wastewater Treatment VII, Proc. of the 10th Gothenburg Symposium 2002*, IWA Publishing, Gothenburg, Sweden, 2002, pp. 17-28.

[21] Gao B-Y., Wang Y., Yue Q-Y., The chemical species distribution of aluminium composite flocculants prepared from polyaluminum chloride (PAC) and Polydimethyldiallylammonium chloride (PDMDAAC), *Acta Hydrochimica et Hydrobiologica*, Vol. 33, No 4, 2005, pp. 365-371.

[22] Gao, B.-Y., Wang, Y., Yue, Q.-Y., Wei, J.-C., Li, Q., Color removal from simulated dye water and actual textile wastewater using a composite coagulant prepared by polyferric chloride and polydimethyldiallylammonium chloride, *Separation and Purification Technology*, Vol. 54, 2007, pp. 157-163.

[23] Zouboulis, A.I., Tzoupanos N.D., Moussas, P.A., Inorganic Pre-Polymerised Coagulants: Current Status and Future Trends, 3rd IASME/WSEAS International Conference, S. Nikolaos, Greece, 24-26 July 2007, pp. 292-300.

[24] Tzoupanos, N.D., Zouboulis A.I., Zhao Y.-C., The application of novel coagulant reagent (polyaluminium silicate chloride) for the post-treatment of landfill leachates. *Chemosphere*, 2008, in press.

[25] Zouboulis, A.I., G. Traskas, Comparable evaluation of various commercially available aluminum-based coagulants for the treatment of surface water and for the post-treatment of urban wastewater, *Journal of Chemical Technology & Biotechnology*, Vol. 80, 2005, pp. 1136-1147.