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Comparative Study of the Effect of Aluminum Chloride, Sodium Alginate and Chitosan on the Coagulation of Polystyrene Micro-plastic Particles

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Abstract

The coagulation of negatively charged polystyrene latex micro-plastic particles is studied in presence of two linear biopolymers (chitosan and sodium alginate) and a trivalent salt, aluminum chloride as coagulants. The performance of the different coagulants, impact of the solution pH, and use of alginate as a coagulant in presence of aluminum chloride, fractal character and compactness of aggregates are investigated by using mainly electrophoretic experiments and image analysis. The coagulant efficiency and coagulation routes and strategies are analyzed by considering the variations of the particle surface charges at variable coagulant concentrations. Optimal coagulant dosage is determined when the surface charge of the latex particle is neutralized.

Our results suggest that the biopolymers are in some cases more efficient than $AlCl_3$ for the destabilization of latex micro-plastic particles. Indeed, charge neutralization is more rapidly achieved by chitosan regarding the optimal dosage and chitosan is found to work over a wider range of pH values. Alginate is also found to be a good candidate when particle charge inversion is achieved first with aluminum chloride. We also demonstrate that coagulant dosage is dependent on the initial pH of the suspension. When the initial pH of the dispersion is low, the isoelectric point is obtained for small dosage values. Image analysis indicates that in all situation fractal aggregates are obtained and that biopolymers result in the formation or more compact structures which will increase the sedimentation rates.

Keywords: water treatment, coagulant dosage, aluminum chloride, chitosan, alginate, latex micro-plastics, charge neutralization

1. Introduction

Coagulation is a common pretreatment procedure used in water treatment plants to remove the natural colloidal or suspended matter by producing aggregates that are large enough to sediment [1-3]. Colloidal particles are usually stabilized by the presence of surface charges (mainly negative) which give rise to repulsions between colliding particles. Destabilization then aggregation between colloidal particles is usually achieved by adding metallic salts or synthetic polymers. Such coagulants are widely used, because they are cheap, effective, produce less residues and are easy to handle [4-5]. However coagulants are not always used in a rational way with regards to the natural fluctuations (e.g., pH, ion strength, and temperature), heterogeneity of water compositions, such as particle concentrations, and their corresponding physicochemical properties [6]. In addition the use of these chemical substances can have several environmental consequences like an increase in metal concentration in water, which may have human health implications [7], and production of large volumes of (contaminated) sludge [8]. Natural polymers may be of great interest since they are natural products, characterized by their environmentally friendly behavior and have the potential to substitute metal based coagulants or synthetic flocculants in water treatment [5]. Among these biopolymers, alginate and chitosan are often considered as the most promising coagulation or co-coagulation materials [5, 9].

Alginate is a linear polysaccharide block copolymer extracted from the cell walls of brown seaweed that comprises 1,4- linked β-D-mannuronic acid and α-L-guluronic acid residues [10]. This biopolymer is widely used in the pharmaceutical and food industry [11], as well as in water treatments. Ngomsik et al. [12] showed the efficiency of Ni^{2+} removal from wastewater with alginate microcapsules. Kawamura [5] also showed the efficiency of the sodium alginate as a co-coagulant with aluminum sulfate (alum) as a primary coagulant in the removal of turbidity. Zhao and al. [13] concluded that sodium alginate used as a co-coagulant can accelerate the rate of the aggregate formation. These results show that such a biopolymer can substitute the anionic synthetic polymers. On the other hand, chitosan is a linear copolymer of D-glucosamine and N-acetyl-D-glucosamine produced by the deacetylation of chitin, a natural polymer of major importance [14]. The potential industrial use of chitosan is widely recognized. This biopolymer is used in biomedical engineering, pharmacy, biotechnology, chemistry, cosmetics, textile, pulp and paper, food industry and agriculture [14]. Because of its positive charges, chitosan is very efficient in interacting with particulate and dissolved substances [15-16,17]. Huang and Chen [18] studied bentonite coagulation by chitosan and concluded that chitosan was an excellent coagulant for bentonite suspensions. Pan and al. [19] investigated the coagulation of synthetic turbid waters using chitosan and polyaluminum chloride (PACl). They concluded that chitosan was a promising substitute for alum and PACl and was able to produce larger flocs of better quality with faster settling velocity.

In colloidal aggregation processes there are two forces to take into consideration. The first concerns the van der Waals forces, which are always attractive and promote aggregation between colloidal particles while the second is related to the repulsive forces, which under unfavorable conditions can overcome the attractive forces and then prevent aggregation [20]. Using inorganic salts, aggregation can be induced by screening effects and charge neutralization mechanisms due to the adsorption of opposite (macro) ions at the particle surface. The electrostatic repulsive forces between the charged colloidal particles can be thus modified by the adsorption of highly charged cations such as Al^{3+} or Fe^{3+}, at the particle surface hence promoting particle attraction [21].

Charged polymers or biopolymers involve different mechanisms [22]. When the molecular weight of the polymer is low in comparison to the particle size, aggregation is promoted by local polymer adsorption and oppositely charged patches are then created which can interact with the particle surface. When the particle surface charge is neutral the electrostatic repulsive forces are canceled, so van der Waals forces, can induce particle aggregation. On the other hand, bridging mechanisms are observed for high molecular weight polymers whose size leads to the formation of extended loops and tails so as to promote the formation of bridges between the particles.

However in both cases, high polymer dosage, prevent aggregation between particles by charge inversion or steric stabilization [23]. Therefore, coagulant dosage is an important parameter to determine for optimal destabilization of colloidal suspensions. Charge density and polymer molecular weight are also important parameters to consider in the understanding of destabilization mechanisms and floc structures for the optimization of the sedimentation rates [24].

The present study compares the efficiency of two linear biopolymers, chitosan and sodium alginate in presence of a trivalent salt, as well as the efficiency of aluminum chloride on the destabilization of negatively charged polystyrene latex particles. In particular the effect of the initial pH suspensions is investigated. Electrophoretic measurements are conducted to determine optimal coagulation conditions regarding initial pH and coagulant dosage. Then aggregate morphologies are examined to obtain the fractal dimension of the resulting structures using image analysis. This study is also addressing indirectly another key and emerging issue which is related to the micro plastic pollution, behavior in presence of various coagulants, and their subsequent removal of aquatic systems including water treatment processes. Indeed field and laboratory work regularly provide new evidence on the presence of plastic debris at the micro-, and potentially also the nano-scale within every aquatic habitat.

2. Materials and methods

2.1. Materials

Polystyrene sulfate latex spheres (Interfacial Dynamics Corporation, USA) are used as a surrogate and model of monodisperse colloidal particles. The original aqueous dispersion contains 78 g/L of negatively charged latex spheres with a diameter equal to 0.99 μm (TEM measurement, provided by the manufacturer). Density and specific surface area are equal to 1.055 g/cm^3 (20 ^{o}C), and 5.7 x 10^4 cm^2/g, respectively. The presence of sulfate groups at the surface results in a constant charge density value equal to 3.9 μC/cm^2 for pH values above 4. We worked with a stock solution of 1 mg/L. This stock solution is used to prepare solutions at well-defined concentrations. Aluminum (III) chloride, $AlCl_3$ is used as a coagulant. A stock solution of 10 mg/L is prepared from $AlCl_3$ anhydrous (Merck, Germany). After dissolution of Al (III) salt hydrolysis reaction can lead to the formation of the many species, such a Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{+}$, $Al(OH)_3$ and $Al(OH)_4^{-}$, which can coexist in solution simultaneously (Fig.1). These reactions and equilibrium constants are given in equations (1)-(4) [2,25,26].

$$Al^{3+} + H_2O \leftrightarrow Al(OH)^{2+} + H^+ \qquad \log K = -4.97 \tag{1}$$

$$Al^{3+} + 2\,H_2O \leftrightarrow Al(OH)_2^{+} + 2\,H^+ \qquad \log K = -9.30 \tag{2}$$

$$Al^{3+} + 3\,H_2O \leftrightarrow Al(OH)_3 + 3\,H^+ \qquad \log K = -15.0 \tag{3}$$

$$Al^{3+} + 4\,H_2O \leftrightarrow Al(OH)_4^{-} + 4\,H^+ \qquad \log K = -21.7 \tag{4}$$

Chitosan of high purity (Sigma Aldrich, Buchs, SG, Switzerland) with a degree of deacetylation DD ≥ 60% and MW 600-1200 Da is also used as coagulant. A 100 mg/L stock solution is prepared and stirred overnight at room temperature. It was necessary to heat this stock solution in a 80 ^{o}C water bath around 20 min to help the dissolution of chitosan then hydrochloric acid was added to the solution until pH 3, and mixed at 100 rpm for 60 min. Low viscosity sodium alginate (Sigma Aldrich, Buchs, SG, Switzerland) is used as co-coagulant. A stock solution of 100 mg/L was prepared and stirred overnight. All the solutions were prepared with deionized Milli Q water (Millipore, Switzerland, with R > 18MΩ.cm). The pH of all solutions was adjusted by adding small amount of diluted HCl and NaOH (Merck, Germany).

2.2. Experimental methods

2.1.1. Zeta potential measurements

The zeta (ζ) potential is related to the electric potential at the boundary surface of the hydrodynamic shear which corresponds to the potential at the slipping plane of the diffuse layer with the bulk solution [27]. The ζ potential is related to particle stability. Highly stable colloidal systems are characterized by high zeta potentials with absolute values > 25mV, whereas low zeta potentials indicate less stable systems.

The Malvern Zetasizer 2000 instrument (Marvel Instruments Ltd, UK) was used to measure the ζ potential values of the latex particles, chitosan, and sodium alginate as well as ζ potential variation of the latex particles as a function of coagulant concentration. For each situation duplicate measurements were performed and each sample was measured five times to determine mean ζ potential values.

2.1.2. Modeling

The MINTEQA2 model is a quantitative tool for predicting the equilibrium behavior of metals in a variety of chemical environments. The program consists of submodels that compute the activities of cationic and anionic species and neutral ion pairs then compute the solubility of solids and minerals and in the end the mass transfer submodel calculates the mass of solid that precipitates or dissolves [28,29].

Using MINTEQA2 software (developed by Allison Geoscience Consultants Inc. and HydroGeologic Inc.), relative concentrations of the aluminum (III) species in solution as a function of initial pH were determined (Fig. 1) for a solution containing 1mg/L of $AlCl_3$ at 25 °C.

Fig.1

2.2.3. Determination of the aggregate fractal dimension D_f

The fractal dimension concept was introduced in the seventies by Mandelbrot [30] so as to describe complex geometrical structures. Structural properties of various objects such as colloidal aggregates can be quantitatively measured applying fractal dimension theory [31]. To determinate the aggregate structures, images were taken with a BX61 microscope (Olympus, Switzerland) then treated with the SigmaScan pro 4 software to calculate the relative mass (in term of total number of pixels) and aggregate dimensions (the major axis lengths). D_f was determinated according to the scaling law relationship [31]:

$$m(r) \approx r^{Df} \tag{6}$$

Where m represents the aggregate mass (number of pixels) and r the aggregate major axis length. D_f of aggregates was calculated by considering a log/log plot of m versus r. In order to validate this method we applied this procedure to solid spheres and lines. D_f values of 1.03 ± 0.05 and 1.99 ± 0.02 respectively were found in good agreement with the theoretical values [32].

3. Results and discussion

3.1. Material characterization

3.1.1. Latex particles

Latex particles zeta potential variation as a function of the pH is shown in Fig 2a. In the pH range investigated the latex particles are negatively charged and no Point of Zero Charge (PZC) is observable. Zeta potential is decreasing to more negative values by increasing the pH. When the pH is above 6 the zeta potential of latex particles is within the range from -75 to -60 mV. For acid environment when pH is below 6, zeta potential values are found smaller, from -50 to -25 mV. Such a behavior is related to the acid-base properties of the surface of the latex particles. Latex particles used in this study are stabilized by the charge of hydrogeno-sulfate groups (pKa < 2). In acid environment sulfate groups start to protonate hence reducing the surface charge. In any case the particles remain highly negatively charged and as a result the suspension is found stable due to the electrostatic repulsive forces in a large pH range from 3.0 to 9.0

Fig.2

3.1.2. Chitosan

Chitosan titration curves of a 100 mg/L stock solution were determined by adjusting pH from 3.0 to 9.0. As shown in Fig. 2b, chitosan exhibits a positive zeta potential value equal to +60 mV at pH 3.0. Amino groups in chitosan molecule are protonated which results to a polymer with positive charges. By increasing pH, a decrease of the surface charge is observed and the PZC is achieved at pH 9.0.

3.1.3. Sodium Alginate

Zeta potential versus pH titration curve of a 100 mg/L sodium alginate suspension is shown in Fig. 2c. Sodium alginate exhibits negative zeta potentials in the pH domain investigated (from 3.0 to 11.0). When the solution pH decreases, zeta potential decreases due to the continuous protonation of the carboxylic groups of the β-D-mannuronate and α-L-guluronate monomers until a value of -13.0 mV in good agreement with the β-D-mannuronate and α-L-guluronate pKa values of 3.2 and 3.6 respectively [33].

3.2. Destabilization of latex particles in presence of AlCl₃

Experiments with a 1 mg/L latex suspension were conducted to evaluate the ability of $AlCl_3$ to destabilize latex particles. Primitive pH of the latex suspension was 5.3. It was then adjusted to 4.0, 6.0, 7.0, 8.0 and 9.0 in other to investigate the influence of the initial suspension pH on the destabilization of latex particles. Zeta potential variations of latex particles as a function of $AlCl_3$ concentration are presented in Fig.3a. In all cases, it is observed that by increasing the $AlCl_3$ concentration the zeta potential is decreased to achieve an isoelectric point (IEP). A further increase in the $AlCl_3$ dosage is found to result in charge inversion.

Fig.3

We also found that the surface charge neutralization was more rapidly achieved at low initial pH values regarding the $AlCl_3$ dosage, in good agreement with the fact that when the pH of the suspension decreases the concentration of positive Aluminum species which are active in the surface charge neutralization increases (Fig. 1) thus resulting in a decrease in $AlCl_3$ dosage. When the pH becomes higher latex particles becomes more negative, resulting in an increase of $AlCl_3$ dosage to neutralize surface charge. It should also be noted that at pH 4 the concentration of cationic species such as Al^{3+} and $Al(OH)^{2+}$ is higher and such conditions should be more efficient for surface charge neutralization. However, as shown in Fig. 3a, at pH 4 the optimal concentration of $AlCl_3$ is higher than expected. This is due to the fact that generally hydrolyzed cationic species such as $Al(OH)^{2+}$ are more strongly adsorbed on negative surfaces than the free hydrated metal ion [34]. Adsorbed metal ions may be in the form of outer sphere complexes, in this case there is at least one water molecule separating the cation from the surface. Inner sphere complexes involve the direct coordination of the metal ion to surface groups with no intervening water [35]. Therefore, the $Al(OH)^{2+}$ species present at low concentration (~10%) are more active in charge neutralization, thus leading to an increase in $AlCl_3$ concentration to achieve the IEP. Strong charge inversion is also observed when the initial pH is equal to 7.0, 8.0 and 9.0. As shown in Fig. 3b, when the initial pH is greater than 6 a significant pH decrease is achieved when adding $AlCl_3$, then pH stabilization is obtained after the IEP. When the pH decreases the relative concentration of positive species of aluminum increases. We hypothesize that positive species of aluminum and dosage increase could explain the strong charge inversion observed at pH 7.0, 8.0 and 9.0.

3.3. Destabilization of latex particles in presence of chitosan

Chitosan efficiency was explored by investigating the zeta potential variations of latex particles at different chitosan dosage (Fig. 4a). Experiments were performed at initial pH values of 3.0 4.0, 5.3, 6.0, 7.0, 8.0, 8.5 and 9.0, using 1 mg/L of latex suspension. In all cases a decrease of the zeta potential was observed by increasing chitosan dosage. Charge inversion was also observed but in this case it was found more pronounced at low pH. We also noted that the optimum chitosan dosage is smaller in acid conditions. This was attributed to the increase in the number of protonated amine groups on chitosan at lower pH [19] and decrease of the latex charge density. In acid environment ($pH<5$) amine groups are mainly protonated and electrostatic repulsions forces promote extended conformations of the biopolymer chain [36].

Fig.4

As a result, electrostatic interactions between amine groups and negative charged latex particles are favored [36], resulting in a decrease in chitosan dosage to achieve the IEP. Important charge inversion is observed in acid environment and becomes less significant by increasing pH. When initial pH value increases, on the one hand the positive charge on chitosan decreases significantly (Fig. 2b) and on the other hand the latex particle negative surface charge become more important. As a consequence, an increase in chitosan dosage is necessary to achieve charge neutralization of latex particles and charge inversion is less important compared to acid environment.

It is important to note that at pH 9 amine groups are deprotonated (Fig. 2b) and the biopolymer cannot neutralize negative charged latex particles. However, Roussy and al. [37] indicated that at this pH precipitation of chitosan and destabilization of latex particles was possible via a bridging mechanism. Such a mechanism requires higher amount of chitosan. On the other hand, we noticed that high concentration of chitosan lead to a decrease in pH as shown in Fig. 4b hence increasing the number of positives charges on chitosan. We believe that without this decrease in pH, surface charge neutralization at pH 9 would not be possible.

The relationships between the optimum $AlCl_3$ and chitosan dosage and initial latex suspension pH, which are illustrated in Fig.5, indicate an optimum $AlCl_3$ dosage range between pH 5 and 7 whereas for the chitosan the optimum dosage is found smaller in acid solutions.

Fig.5

Compared to $AlCl_3$, chitosan is more efficient in the destabilization of the latex particles. Surface charge neutralization is more rapidly achieved by chitosan regarding the optimal dosage of both coagulants. Above the optimal dosage, strong charge inversion is observed with $AlCl_3$ while chitosan results to a charge inversion which is less important. This is an important point indicating that an excess of chitosan will not re-stabilize the suspension via electrostatic repulsions. When charge neutralization is achieved a fraction of $AlCl_3$ remains as residual dissolved aluminum in solution. When pH > 7.0, the residual Al concentration increase linearly, which is caused by the high concentrations of $AlCl_3$ added to the solution, resulting in a high content of monomers positively charged in solution at basic pH [38]. Therefore control of the solution pH and $AlCl_3$ dosage is a very important issue for minimizing the residual Al concentrations.

3.4. Destabilization of latex particles in presence of sodium alginate

Experiments with sodium alginate were performed at pH 8.0 which corresponds to the usual pH of the aquatic systems and by considering a 1 mg/L concentration of latex particles. When sodium alginate was used alone as a simple flocculant no change in the latex particle zeta potential was observed and a constant value was obtained at -50 mV (Fig.6a). Both latex particles and sodium alginate are negatively charged with zeta potential values of -51 and -30 mV respectively. As a result, the latex particles remain stable due to the electrostatic repulsion between them and alginate.

Fig.6

Then we investigated the effect of sodium alginate used as a co-coagulant with $AlCl_3$ as primary coagulant. Sodium alginate was added 30 s after the primary coagulant addition. Dosages corresponding to 0.05, 0.1 and 0.2 mg/L were selected for $AlCl_3$, which correspond to $AlCl_3$ concentrations lower and higher than the charge neutralization concentrations. The results are presented in Fig. 6a. When sodium alginate is used in combination with 0.05 mg/L of $AlCl_3$ no significant change in the zeta potential is observed with increasing the alginate concentration. On the other hand surface charge neutralization is observed when 0.1 mg/L of $AlCl_3$ is added to the solution. Then the zeta potential which was close to zero decreases to -7 mV approximately after addition of sodium alginate, hence denoting limited alginate adsorption. By increasing further $AlCl_3$ concentration, significant charge surface inversion is observed when 0.2 mg/L of $AlCl_3$ is added to the solution (Fig. 6b). Then after addition of sodium alginate, zeta potential decreases to zero then charge inversion is observed. These results are important and indicate that alginate could be used as an efficient co-coagulant in particular when charge neutralization and charge inversion of latex particles are achieved with the addition of $AlCl_3$.

3.5. Determination of the aggregate fractal dimension D_f

In other to check the fractal character and compactness of aggregates in presence of salt and biopolymer, aggregates were collected after 180 min of mixing at 350 rpm and at optimal $AlCl_3$, chitosan and sodium alginate dosage (respectively: 0.3, 0.1 and 0.017 mg/L). For each situation 3 samples of latex suspension (100 mg/L) at pH 5.4 were analyzed.

Fig.7

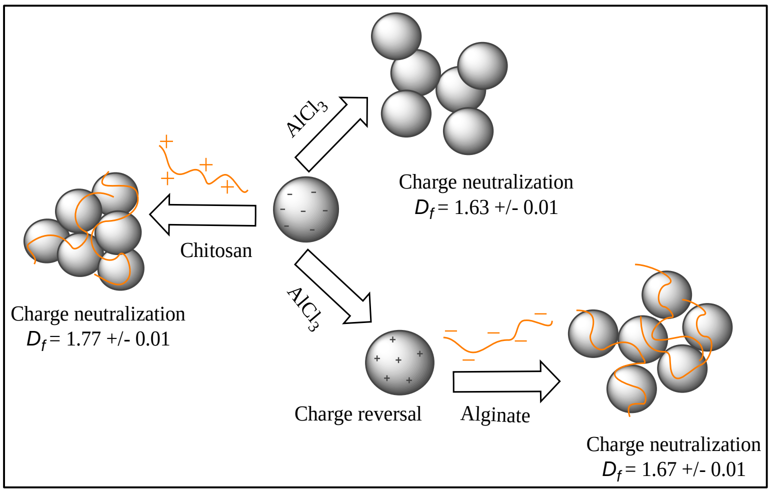
In Fig. 7 is presented on log-log plots the variation of the aggregate masses as a function of their major axis length for $AlCl_3$, chitosan and sodium alginate. Pictures corresponding to the resulting aggregates are shown in Fig. 8. It is interesting to note that aggregates induced by $AlCl_3$ exhibit a D_f value of 1.63 ± 0.01 in good agreement with values found for the cluster-cluster aggregation model for the diffusion limited aggregation process (DLA) which result in the formation of open structures. Higher D_f values were observed (D_f = 1.67 ± 0.01 and 1.77 ± 0.01 respectively) for sodium alginate and chitosan denoting that these aggregates were more compact, in particular when chitosan is used.

Fig.8

4. Conclusions

Our results indicate that different strategies can be used for the aggregation then elimination of suspended particles in water and that in all case coagulant dosage and initial pH are important parameters to consider. Coagulant dosage is expected to be dependent on the initial pH and from a general point of view less coagulant is required to achieve particle surface charge neutralization when low pH dispersions considered. Also coagulant charge and speciation are important issues to consider when efficient particle coagulation is desired.

Our findings suggest that chitosan efficiency is comparable to $AlCl_3$ efficiency and could be considered as an efficient substitute. On the other hand alginate is also an interesting candidate when charge inversion is achieved with an excess of metallic coagulant. Another interesting result of this study is the resulting structures of the formed aggregates. Differences on fractal dimension between the two biopolymers and the metal salt were observed, denoting that the aggregates formed by the biopolymers are more compact hence giving much higher sedimentation rates and therefore improving solid-liquid separation processes.



Graphical abstract

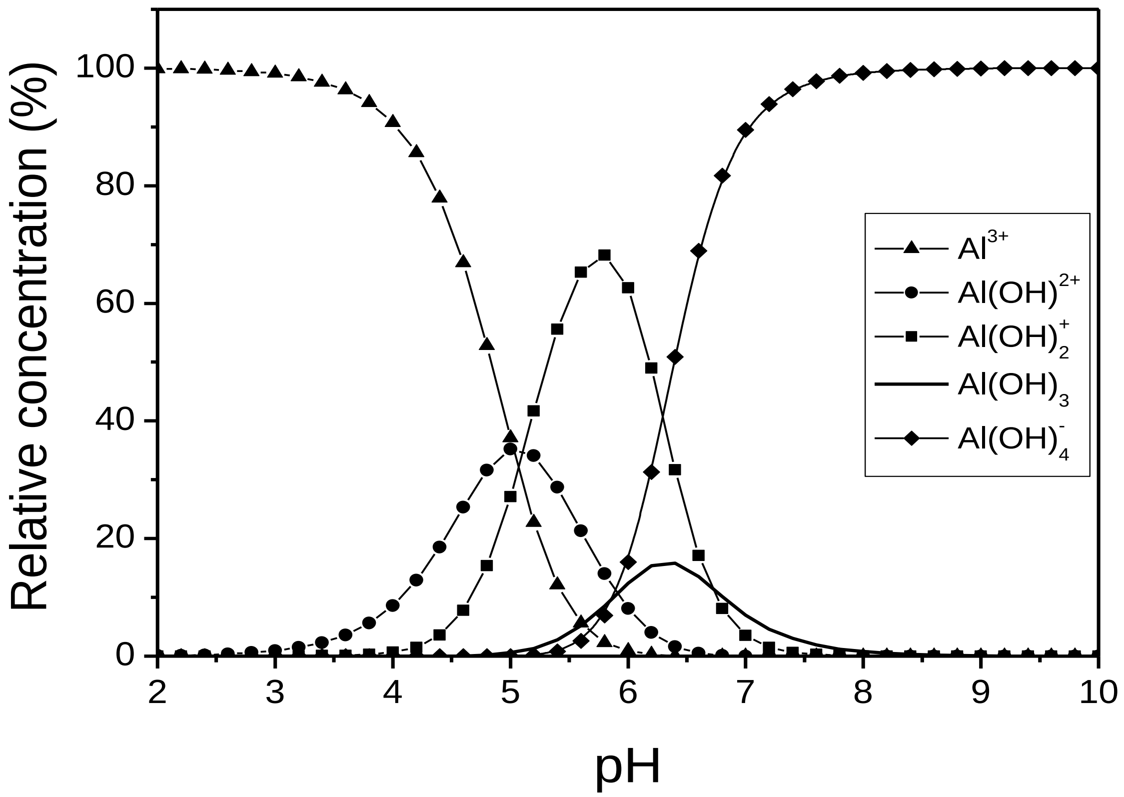


Fig. 1. **Speciation of aluminum (III) as a function of pH for a 1 mg/L $AlCl_3$ solution. Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2^+$ are mainly present in solution at pH 5. At pH 6 and 6,5 the highest relative concentration is obtained for $Al(OH)_2^+$ and $Al(OH)_3$ respectively. When pH is higher than 7, $Al(OH)_4^-$ is mainly present.**

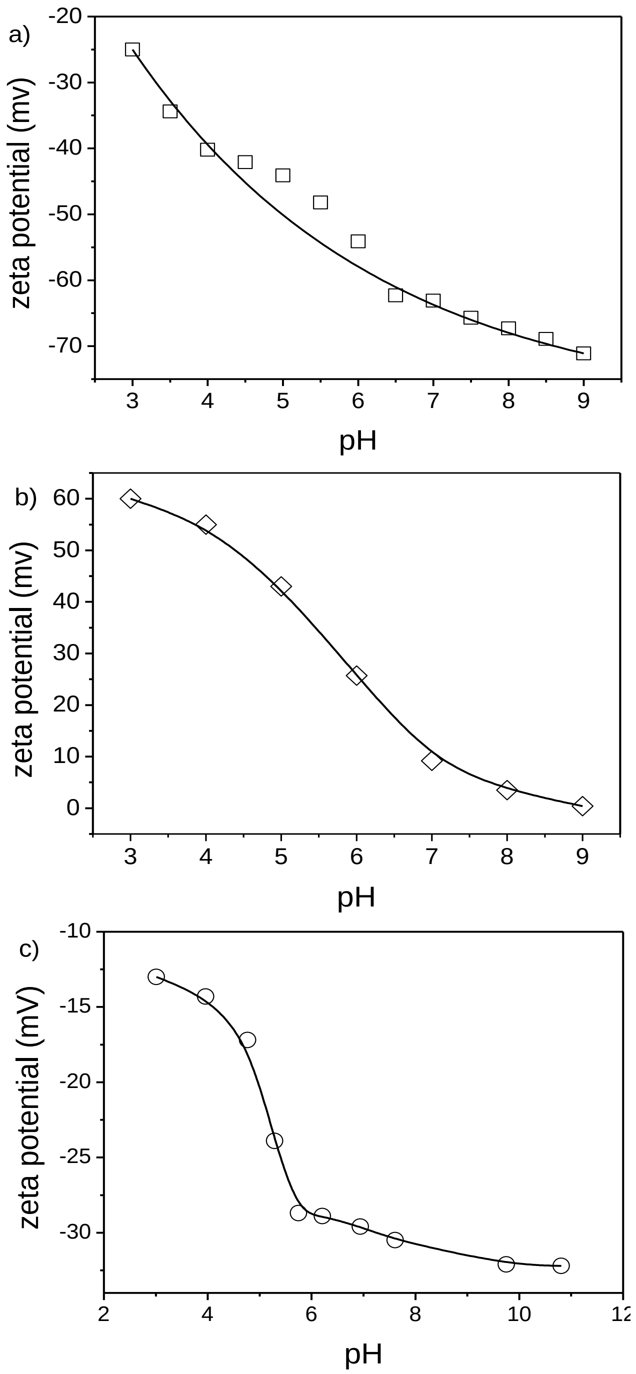


Fig. 2. **Zeta potential variation of a) □ sulfate latex particles as a function of pH. Latex particles are negatively charged in the investigated pH range. They are found stable (no aggregate formation). [Latex] = 1 mg/L. b) ◊ chitosan as a function of pH. Despite a significant decrease with pH increase chitosan remains positively charged in the investigated pH domain. pH$_{PZC}$ is found equal to 9.0 ± 0.1. [Chitosan] = 100 mg/L. c) ○ sodium alginate as a function of pH. Sodium alginate is negatively charged in the investigated pH range. [Alginate] = 100mg/L.**

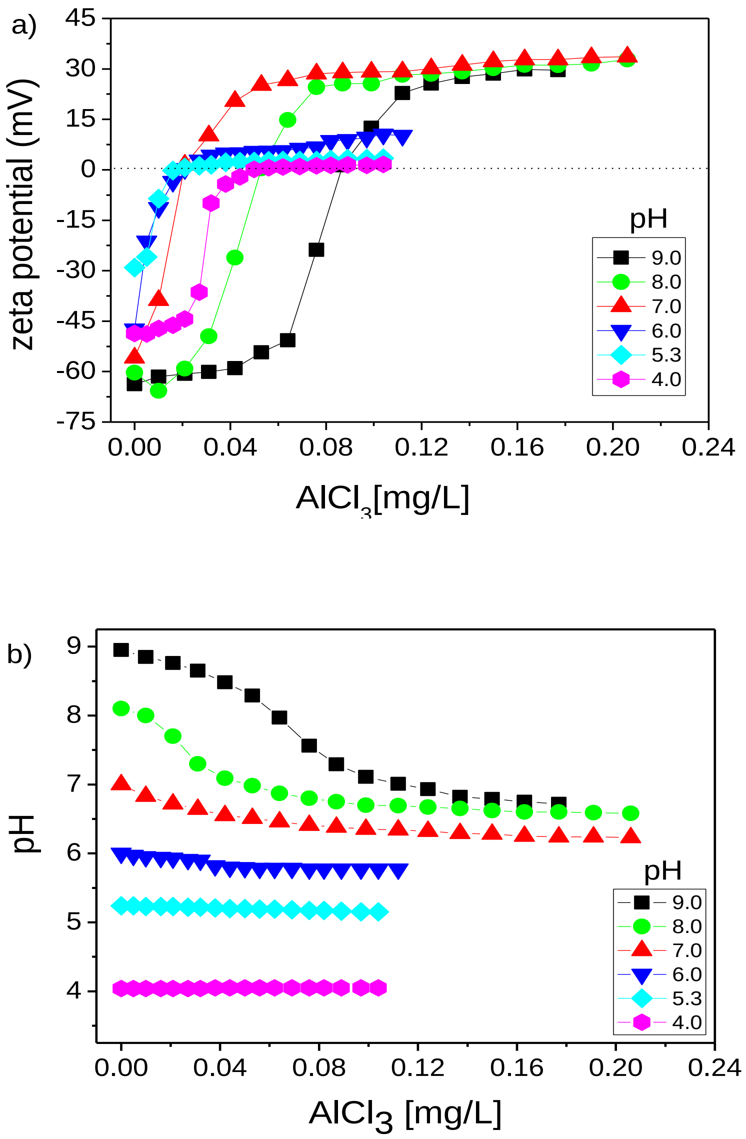


Fig. 3. **a) Zeta potential variation of sulfate latex particles as a function of $AlCl_3$ concentration (successive additions) at different initial pHs. It is found that by increasing the initial pH, surface charge neutralization requires higher coagulant dosage. b) Initial pH fluctuation of sulfate latex particles as a function of $AlCl_3$ concentration. A decrease of pH is observed by increasing $AlCl_3$ concentration (excepted at pH 4, where pH increases with $AlCl_3$ dosage). It is found that pH fluctuation is more significant for basic solutions.**

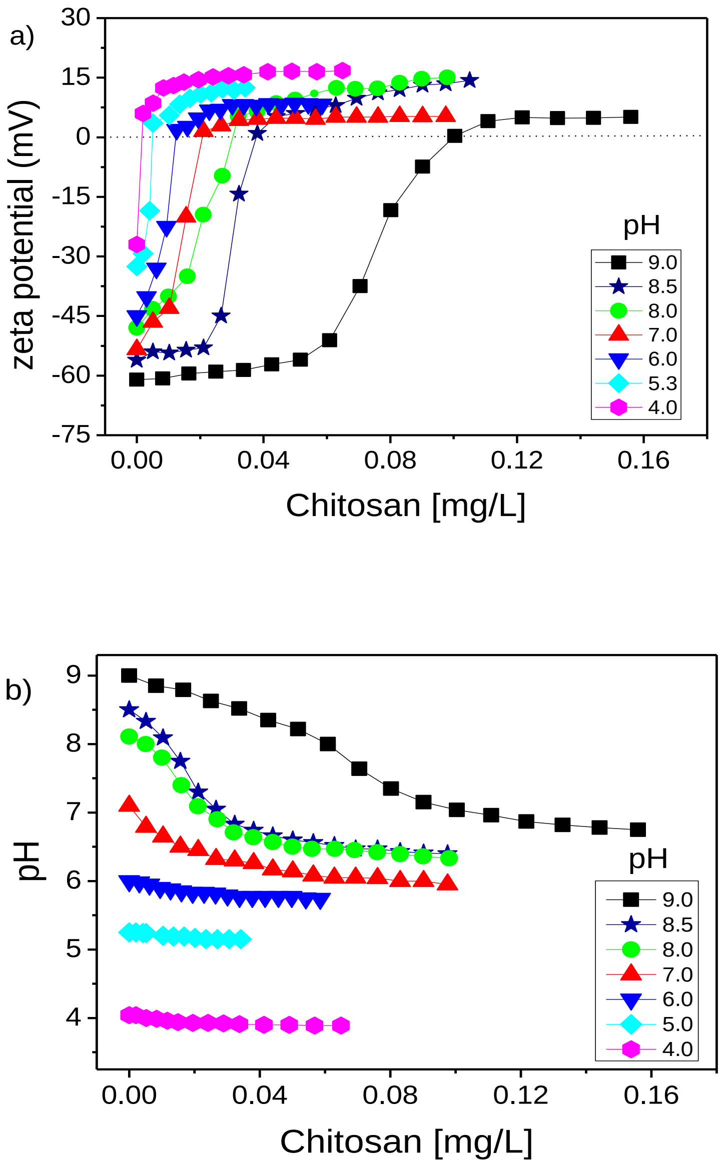


Fig. 4. **a) Zeta potential variation of sulfate latex particles as a function of chitosan concentration (successive additions) at different initial pHs. It is found that by increasing the initial pH, surface charge neutralization requires higher concentration of chitosan molecules. b) Initial pH fluctuation of sulfate latex particles as a function of chitosan concentration. In all case a decrease of pH is observed by increasing chitosan dosage. It is found that pH fluctuation is more significant for basic solutions.**

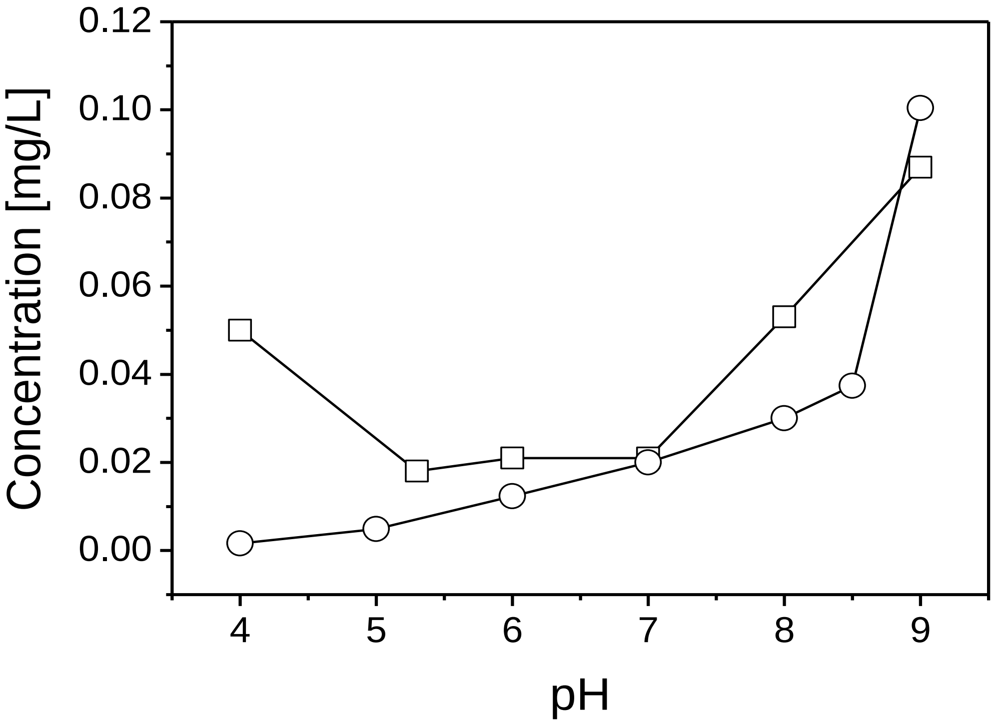


Fig. 5. **Optimal concentration of (□) $AlCl_3$ and (○) chitosan to achieve the latex particles surface charge neutralization as a function of initial pHs. It is found that the optimum chitosan dosage is smaller at low pH. $AlCl_3$ show an optimum dosage range between pH 5 and 7 whereas chitosan optimum dosage range is larger. In both curves by increasing pH a significant increase of coagulant is necessary.**

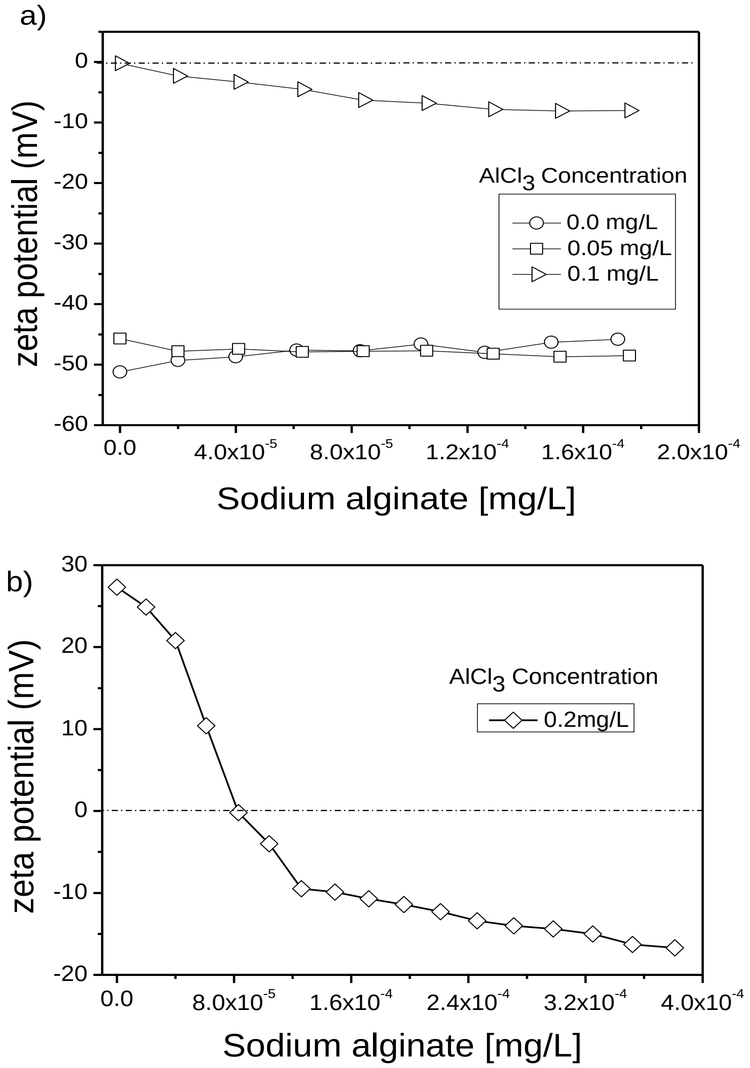


Fig. 6. **Zeta potential variation of sulfate latex particles as a function of sodium alginate concentration a) in presence of different Al (III) chloride concentration b) in presence of 0.2 mg/L of $AlCl_3$ concentration (successive additions) at pH 8.0 ± 0.1. It is found that alginate can serve as an efficient co-coagulant when first a significant charge inversion is achieved with $AlCl_3$.**

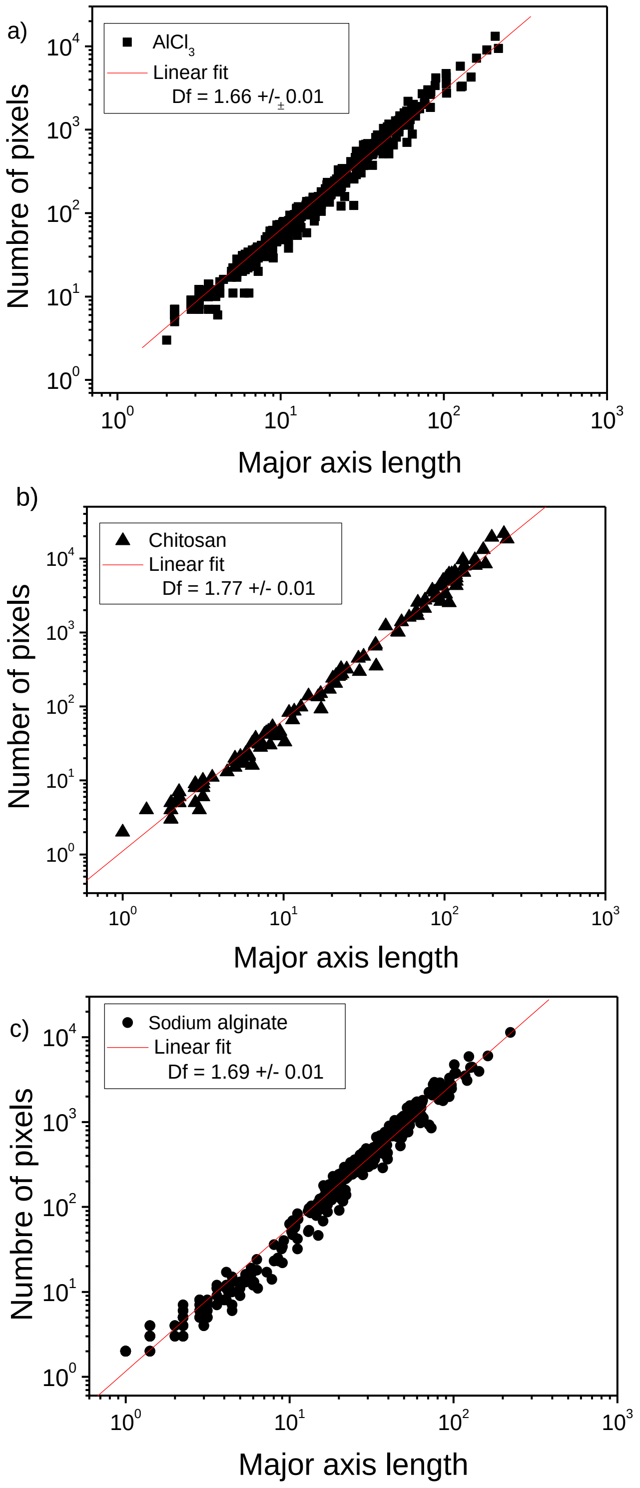


Fig. 7. **Log-log plot of the number of pixels as a function of major axis length for aggregates obtained by destabilization of latex suspensions after 180 min with: a) $AlCl_3$, b) chitosan, c) sodium alginate. Average D_f values obtained by analyzing 3 pictures of each solution. D_f values correspond to 1.63 ± 0.01 for $AlCl_3$, 1.67 ± 0.01 for $AlCl_3$-sodium alginate and 1.77 ± 0.01 for chitosan.**

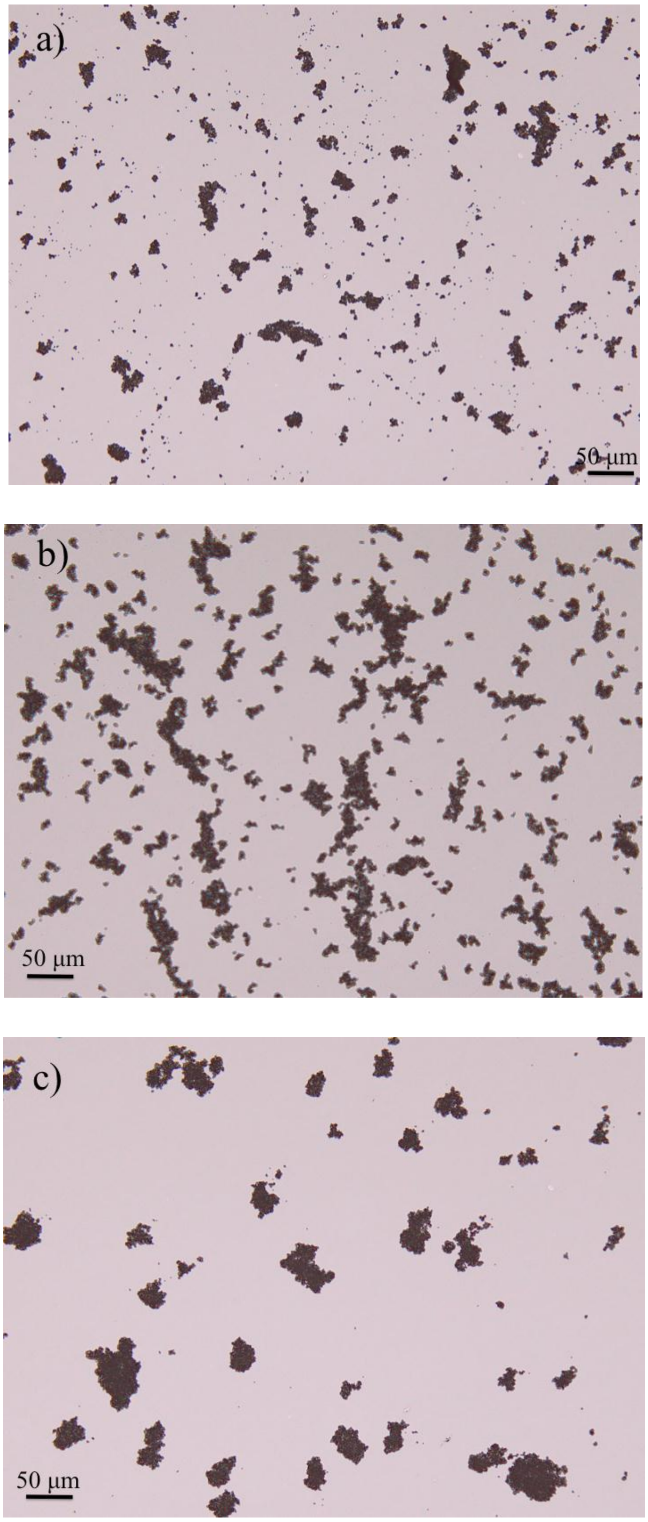


Fig. 8. **Aggregate pictures obtained by destabilization of latex suspensions after 180 min with: a) $AlCl_3$, b) $AlCl_3$-sodium alginate c) chitosan. Aggregates obtained with $AlCl_3$ are found to exhibit open structures, large and branched structures are observed for $AlCl_3$-sodium alginate. Aggregates obtained with chitosan are more compacts and more monodisperse.**

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