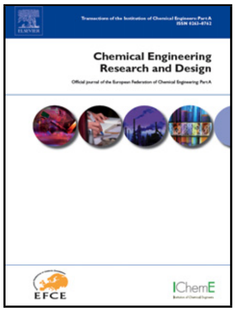

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PII: S0263-8762(14)00484-5
DOI: http://dx.doi.org/doi:10.1016/j.cherd.2014.11.007
Reference: CHERD 1738

To appear in:

Received date: 28-6-2014
Revised date: 8-11-2014
Accepted date: 13-11-2014

Please cite this article as: Rasteiro, M.G., Pinheiro, I., Ahmadloo, H., Hunkeler, D., Garcia1, F.A.P., Ferreira, P., Wandrey, C.,Correlation between flocculation and adsorption of cationic polyacrylamides on precipitated calcium carbonate, *Chemical Engineering Research and Design* (2014), http://dx.doi.org/10.1016/j.cherd.2014.11.007

Correlation between flocculation and adsorption of cationic polyacrylamides on precipitated calcium carbonate

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HIghlights

- Influence of C-PAM characteristics on adsorption on PCC particles was evaluated
- The Langmuir isotherm model describes well the experimental adsorption results
- Correlation between adsorption and kinetics of the 1st flocculation stage was found
- Floc structure correlates with maximum amount of C-PAM adsorbed on particles surface

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Abstract

The study of each stage of the flocculation process is essential to better understand and predict flocculation mechanisms. The adsorption of cationic polyacrylamide derivatives (C-PAM) onto precipitated calcium carbonate (PCC) has been investigated systematically as a function of the C-PAM characteristics including molar mass, chain architecture, and charge density. The adsorption results show that, for C-PAM of similar molar mass, highly branched architectures reach the equilibrium faster than linear C-PAM. Similarly, the flocculation rate is higher for the branched C-PAM, which may be indicative of the predominance of the bridging mechanism. In terms of the molar mass, lower molar mass leads to lower adsorption rates and slower flocculation. Adsorption isotherms of C-PAM onto precipitated calcium carbonate could be described by the Langmuir isotherm model. The maximum amount of C-PAM that adsorbs on the particle surface as a monolayer, obtained from adsorption tests through the Langmuir isotherm linear fit, could be correlated with the structure of the aggregates, obtained from flocculation experiments. Moreover, a good correlation was obtained between the adsorption results and the kinetics of the first stage of the flocculation process dominated by particle aggregation.

Keywords: Cationic polyacrylamide, Flocculation, Flocculation mechanisms, Adsorption, Langmuir isotherm

1. Introduction

Many different synthetic and natural chemical additives are used in the paper industry during the wet end formation process, for a variety of different reasons. Fillers are commonly used to improve process efficiency and the paper properties including opacity, brightness, sheet formation, smoothness and dimensional stability (Gaudreault et al., 2009 and Sung-Hoon and Xin-Sheng, 2006). Additionally, in order to retain the fine particles in the fiber web, polyelectrolytes (PEL) are widely used as flocculants serving as retention or drainage aids (Nasser et al., 2013).

The dynamics of the flocculation process involves the adsorption of the polymer onto the particle surface. Thereafter, for partially covered surfaces, the polymer already adsorbed on a given particle may attach to the bare surface on another particle forming bridges (bridging flocculation**)** or, alternatively, through patching and charge neutralization mechanisms (Gregory, 1989 and Gaudreault et al., 2009). Furthermore, in turbulent environment, flocs can break-up. After flocs break up, the polymer chains can re-conform on the particles surface and subsequently re-attach to other particles or aggregates due to collisions between the particles. Each of these processes depends on the polyelectrolyte and particle characteristics, on the contact time, and on the turbulence intensity (Gregory, 1985; Berlin and Kislenko, 1995 and Biggs et al., 2000).

The separate study of each stage of flocculation permits a better understanding of the different flocculation mechanisms. A reliable correlation between flocculation and adsorption processes can help to control flocculation and, as a consequence, to enable tuning the process with the goal to obtain the desired floc characteristics. One factor, which determines the efficiency of the polyelectrolytes as retention aids, is their conformation at the surface on which they adsorb. This conformation depends on the charge density, the molar mass, as well as on the chain architecture of the polyelectrolyte, though also on the ionic strength of the medium and on the surface charge/charge density of the particles (Defeijter et al., 1978 and Stemme et al., 1999).

High molar mass polyelectrolytes act mostly according to a bridging mechanism (Gregory, 1985 and 1989, Sung-Hoon and Xin-Sheng, 2006 and Rasteiro et al., 2008), the PEL molecules forming a long link between particles. The adsorbed molecule must exhibit an extension from the particle surface which is at least of the same magnitude as the distance between the particles, which is often governed by the thickness of the electrical double layer. Although polyelectrolytes may have an extended conformation in solution this does not mean that the chain is extended when adsorbed to a surface (Gaudreault et al., 2009). Upon adsorption to a surface, interactions come into force, which frequently alter the polyelectrolyte conformation. At low ionic strength, a highly charged polyelectrolyte will have an extended conformation in solution but can have a rather flat conformation on an oppositely charged surface (Gaudreault et al., 2009). In general, highly charged polyelectrolytes and/or low molar mass polyelectrolytes will act mainly according to the bare patch mechanism, which leads, eventually, to charge neutralization (Gregory 1985 and Blanco et al., 2002).

At equilibrium, the amount of a polyelectrolyte adsorbed on a charged surface depends on the properties of the polyelectrolyte, particle, and medium. These include the concentration and solubility of the polymer, the physical and chemical affinity of the polyelectrolyte to the surface, the surface charge density of the particles, and the ionic strength of the medium. Other parameters, which can also influence this process, are the temperature and pH, which can have an impact on the charge of both polyelectrolyte and surface and on the ionic strength (Gregory, 1973 and 1988, Soldberg and Wagberg, 2003).

The objective of this study was to correlate adsorption and flocculation induced by cationic polyelectrolyte (C-PAM), while varying the molar mass, chain architecture and charge density of the C-PAM, in order to deeper understand the relation between the two processes. The work focussed on applications of industrial interest, since adsorption studies dealing with imperfect particles, as the ones present in industrial processes, are still scarce. In the present paper, the interest was directed to papermaking. Therefore, precipitated calcium carbonate (PCC) was used in the flocculation and adsorption tests. Precipitated calcium carbonate particles are far from being spherical and possess a wide size distribution. Besides papermaking, precipitated calcium carbonate is used, for example, in paints, plastics and other coatings, or materials for medical implants.

According to several authors, the amount of polyelectrolyte adsorbed at equilibrium and the extent of surface coverage of the particle by the molecules is the governing variable determining the flocculation mechanism (Zhou and Franks, 2006; Hogg, 1999 and Peng and Garnier, 2010). Furthermore, it has been shown that the effectiveness of flocculation strongly depends on the mixing intensity, how fast the polyelectrolyte comes into contact with the particles. This reinforces the importance of the adsorption rate to the flocculation process (Hogg, 1999).

Laser Diffraction Spectroscopy (LDS) was used to monitor the flocculation process in turbulent conditions, supplying information on the flocculation kinetics and the floc structure (Rasteiro et al., 2008). Good correlation was obtained between the adsorption results and the kinetic data of the first stage of the flocculation process, which is dominated by particle aggregation.

2. Materials and Methods

2.1. Materials

The flocculation and adsorption tests were carried out on a commercial scalenohedral precipitated calcium carbonate suspension, supplied by OMYA and prepared at 1% (w/w) in distilled water. In order to obtain a good dispersion of the particles, the suspension was first magnetically stirred for 20 min and then submitted to sonication at 50 kHz during 15 min. After this treatment, the median size of the particles, measured by Laser Diffraction Spectroscopy, was 2.05 μm and the suspension pH was 8.5. The zeta potential of the particles was -32 mV in distilled water, measured in the Zetasizer Nano-ZS (Malvern Instruments).

Cationic polyelectrolytes, copolymers of acrylamide and acryloyloxyethyl-trimethylammonium chloride (C-PAM), of different molar mass, chain architecture and charge density, supplied by AQUA+TECH, Switzerland, were used for the adsorption and flocculation experiments. Table 1 presents a summary of the cationic flocculants tested.

Table 1. Cationic flocculants provided as emulsions with 40% polyelectrolyte content [a]

Copolymer	Molar Mass Classification	Level of Branching[b]	Cationic Content (wt%)[a]
E1	High	linear	~ 45
E1++++	High	4	~ 45
E2	Medium	linear	~ 45
E2++++	Medium	4	~ 45
F1	High	linear	~ 35
F1++++	High	4	~ 35

[a] information in this Table has been provided by the supplier

[b] the number refers to the equivalent of crosslinker added during the synthesis (Hernandez Barajas et al., 2001, 2003a and 2003b).

2.2. Methods

1. Polyelectrolytes characterization

The intrinsic viscosity (IV) of the isolated and redissolved copolymers was determined in 0.05 M NaCl aqueous solution at 20 ± 0.1°C by dilution viscometry, using an automatic capillary viscometer Viscologic TI1 (Sematech, France), capillary 0.58 mm. The extrapolation to zero concentration was performed according to, Schulz-Blaschke as described elsewhere (Bourdillon et al., 2006). The composition of the copolymers was verified by potentiometric titration and FTIR spectroscopy (Chimankpam et al., 2011). Molar mass analyses were performed by sedimentation velocity experiments in an analytical ultracentrifuge OPTIMA XL-I (Beckman Coulter, Palo Alto, USA) as described previously (Bourdillon et al., 2006).

1.1.1. Flocculation tests

Laser Diffraction Spectroscopy (LDS) was used to monitor the flocculation process in turbulent conditions. Laser Diffraction Spectroscopy supplies information about the flocculation kinetics and, simultaneously, on the evolution with time of the floc structure. The tests were conducted in a Malvern Masterziser 2000 (Malvern Instruments). The precipitated calcium carbonate suspension was added to 700 mL of distilled water in the equipment beaker until a fixed level of obscuration was obtained corresponding to an average precipitated calcium carbonate concentration of 0.05% (w/w). The tests were carried out at a stirring speed of 1400 rpm, corresponding to an average shear rate of 312 s^{-1} in the vessel. This procedure has been described in detail elsewhere (Rasteiro et al., 2008 and Rasteiro et al., 2011). Flocculants were tested for a range of concentrations. The reported values of the average particle size ($D_{4,3}$) represent an average of at least four replications (maximum deviation 5%).

Two regions corresponding to different kinetics can be identified in the flocculation curve: a first one dominated by particle aggregation (kinetic constant k_1); and a second one dominated by floc stabilization due to the balance between aggregation and breakage (kinetic constant k_2). This is schematically shown in Figure 1. The shape of the flocculation curve depends on the predominant flocculation mechanism. If bridging is the principal mechanism, flocs suffer restructuring after the initial aggregation step, as the polyelectrolyte molecules possess a higher degree of freedom to reconform on the particle surface. On the contrary, when bare patch attraction is the main mechanism reconformation of the polymer molecules becomes difficult and restructuring is not observed on the flocculation curve, as schematically shown in Figure 1.

A mathematical model was fitted to the curves enabling the computation of the kinetic constants for both regions (Rasteiro et al., 2008).

$$D_{4,3} = Ae^{k_1 t} \tag{1}$$

Where A is a pre-exponential factor (μm), t is the time (min) and k_1 is the kinetic constant for the first region (min^{-1}).

$$D_{4,3} = Ae^{1/k_2 t} \tag{2}$$

Where k_2 is the kinetic constant (min^{-1}) for the second region.

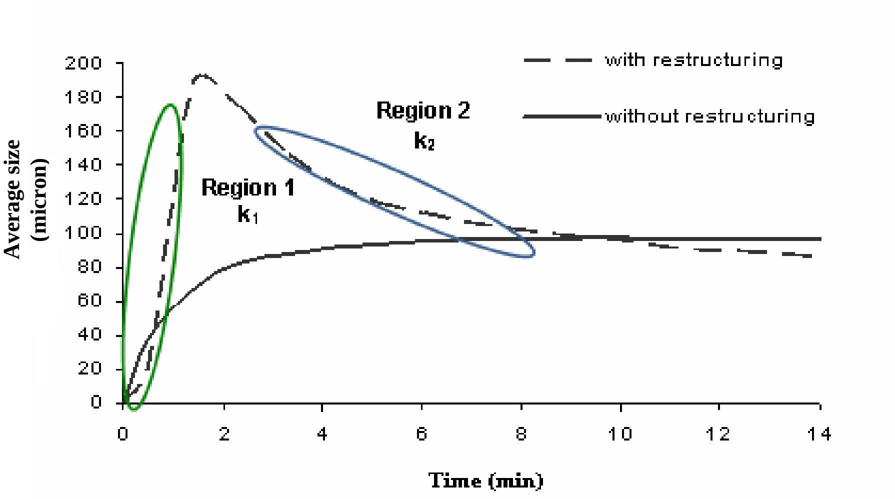


Figure 1. Schematic diagram of typical flocculation kinetic curves.

1.1.2. *Adsorption tests*

Adsorption isotherms of polyelectrolytes were determined as follows: 700 mL of precipitated calcium carbonate suspension with different PEL dosages were stirred using the same conditions as during the flocculation tests, 1400 rpm, at room temperature (22 ºC). The contact time was controlled to be between 16 to 60 min. The dosage of C-PAM was varied in order to guarantee that complete surface coverage was reached. The concentration of the C-PAM in the supernatant solutions was analyzed by UV/vis spectroscopy at 300 nm (Deng et al., 2006). A calibration curve was produced for each polyelectrolyte using five solutions of different known concentrations.

The amount of C-PAM (Q_e) adsorbed onto the precipitated calcium carbonate (mg C-PAM/g PCC), was calculated from the initial and final C-PAM concentrations (Tekin et al., 2005 and Tekbas et al., 2009) based on the mass balance described by Eq. (3):

$$Q_e = (C_0 - C_e)\,\frac{m_{PCC}}{V_{C-PAM}} \qquad (3)$$

Where C_0 and C_e are the initial and equilibrium liquid-phase concentrations of C- PAM (mg/L), respectively, V the volume of the C- PAM solution (L), and m_{PCC} is the mass of the precipitated calcium carbonate sample used (g).

3. Results and discussion

3.1. *Polyelectrolytes characteristics*

Table 2 presents the results of the polyelectrolytes characterization.

Table 2. PEL characterization.

Copolymer	Cationic Content (wt%)	IV_{SB}, 0.05 M NaCL (ml/g)^c	$M_{s\eta} \times 10^{-6}$ (g/mol)^d

E1	45.5	2490	1.9
E1++++	42.8	1772	------
E2	47.3	1550	1.3
E2++++	43.2	977	------
F1	34.2	1399	3.6
F1++++	34.4	914	------

[c] according to Schulz-Blaschke

[d] as described in Bourdillon et al., 2006.

The composition analysis confirmed the intended differences of the E and F samples within acceptable ranges. This allows for studying the influence of the charge density for polyelectrolytes of similar molecular size and architecture.

Evaluating the impact of the molar mass and the chain architecture on adsorption and flocculation, the following facts have to be considered in general and for the copolymers used here: for the same molar mass and chemical composition (cationic content), the intrinsic viscosity, as a measure of the hydrodynamic dimensions, decreases with increasing degree of branching (Burchard, 1999). This is confirmed by the values in Table 2 for the series E1, E2 and F1. While the influence of the chain architecture on the IV-molar mass relationship is relatively well understood for neutral polymers, this is not the case for charged macromolecules. It is however known that the ionic strength has a stronger influence on the hydrodynamic dimensions of linear PEL than on branched ones. Further, polylectrolytes of lower charge density are less extended in the same medium than those with higher charged density but having the same molar mass. This is confirmed comparing F1 with E1 and E2. Despite the even higher molar mass of

F1, the intrinsic viscosity is lower. Overall, the intrinsic viscosity can be considered as a more appropriate correlation parameter for the comparison of PEL of different molar mass, composition and chain architecture, in terms of their adsorption behavior and flocculation performance. The molar mass values in Table 2 are therefore intended to provide an order of magnitude only. As observed previously (Bourdillon et al., 2006) highly branched samples of this copolymer type can contain a very fast sedimenting fraction, which is in 0.05 M NaCl at its solubility limit. The molar mass could therefore not be determined for the highly branched polyelectrolytes as for the other samples, and is thus not meaningful for comparison. IV values, to which all molecules contribute, are more suitable.

Nevertheless, based on the sample characteristics in Table 2, the influence of the macromolecule size, charge and architecture can be estimated while comparing E1 and E2 as well as E1++++ and E2++++ concerning the influence of the IV/molar mass; comparing linear and branched samples of the E1, E2 and F1 series concerning the influence of the architecture; and comparing the linear and the respective branched E and F samples concerning the charge density.

3.2. Adsorption of C-PAM on precipitated calcium carbonate particles

Figure 2 gives an example of a calibration curve. For all the calibration curves, the correlation coefficients R^2 were always > 0.99.

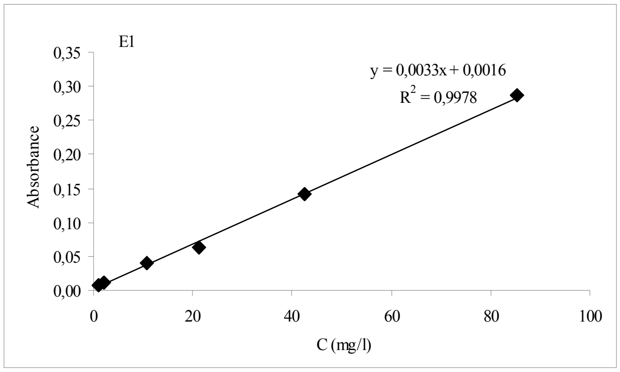
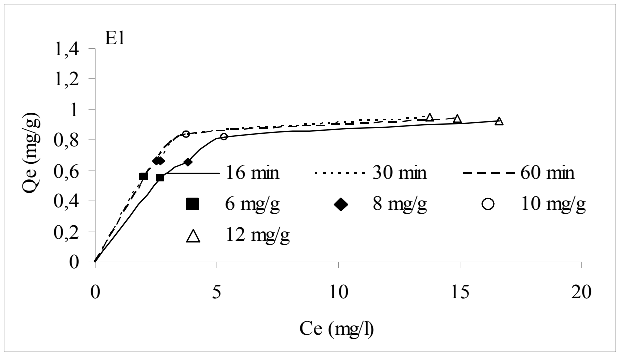
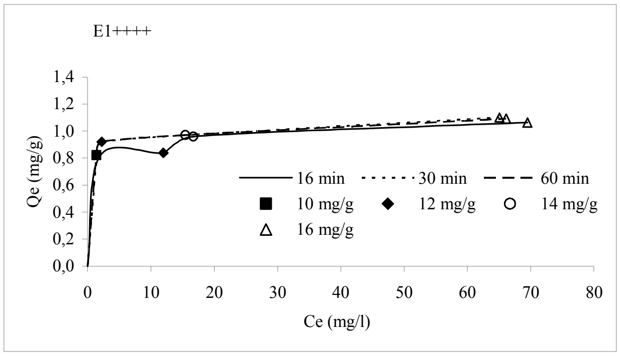


Figure 2. Calibration curve for E1**.**

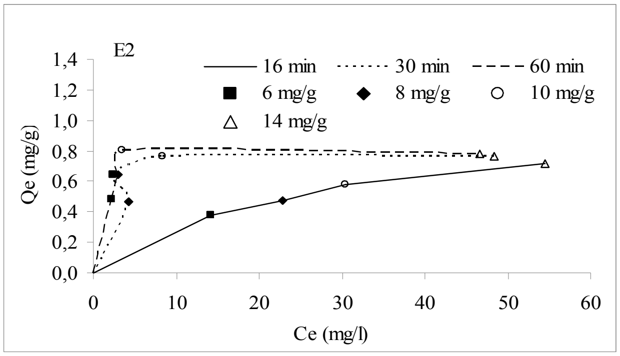
In Figure 3, all the experimental adsorption curves are presented as the amount of C-PAM adsorbed per unit mass of precipitated calcium carbonate (Qe, mg/g) as function of the equilibrium C-PAM concentration (Ce, mg/l). Each graph shows the curves for the three different contact times tested, 16, 30 and 60 min. For each contact time, four initial polyelectrolyte concentrations have been tested. On each equilibrium isotherm, the four or five different symbols correspond to different initial polyelectrolyte concentrations in the range of 4 to 18 mg C-PAM/g PCC. The range of these initial concentrations is identical with the range used in the flocculation tests.



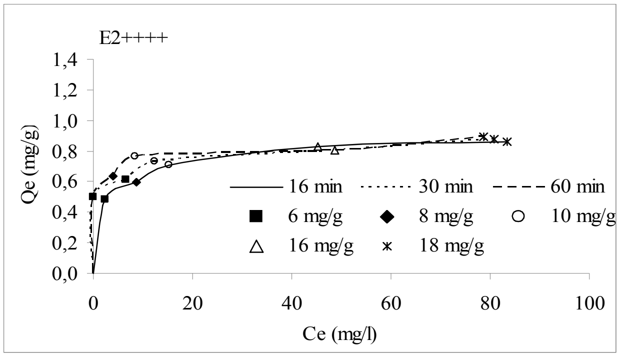
(a)


E1++++
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0,0
Qe (mg/g)
0
10
20
30
40
50
60
70
80
Ce (mg/l)
16 min
30 min
60 min
10 mg/g
12 mg/g
14 mg/g
16 mg/g

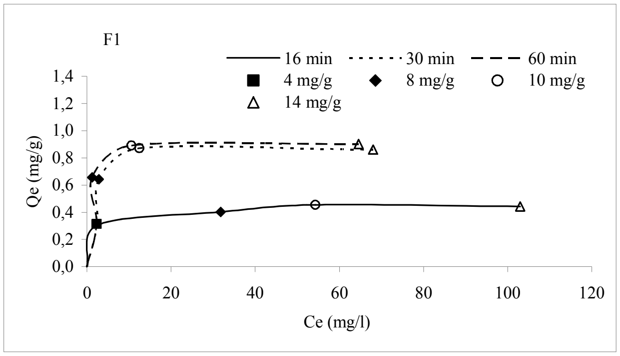
(b)


E2
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0,0
Qe (mg/g)
0
10
20
30
40
50
60
Ce (mg/l)
16 min
30 min
60 min
6 mg/g
8 mg/g
10 mg/g
14 mg/g

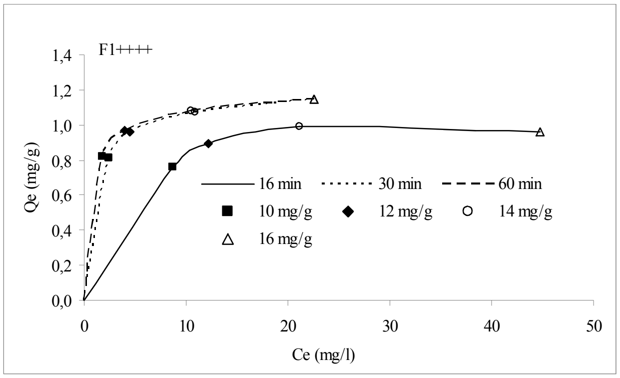
(c)


E2++++
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0,0
Qe (mg/g)
0
20
40
60
80
100
Ce (mg/l)
16 min
30 min
60 min
6 mg/g
8 mg/g
10 mg/g
16 mg/g
18 mg/g

(d)



(e)



(f)

Figure 3. Adsorption of C – PAMs on precipitated calcium carbonate for different contact times: E1 (a), E1++++ (b), E2 (c), E2++++ (d), F1 (e), F1++++ (f).

In all experiments summarized in Figure 3, a contact time above which no more polyelectrolyte could be adsorbed on the particles can be identified. This time depends on the polyelectrolyte characteristics.

Additionally, in Figure 4, the C-PAM adsorption kinetic curves, for a common concentration of 10 mg of C-PAM/g PCC and for the different polyelectrolytes studied, are presented.

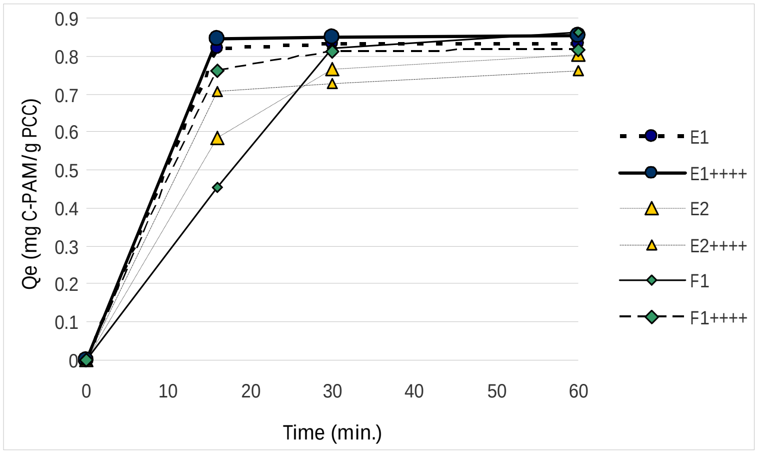


Figure 4. Adsorption kinetic curves for the different polyelectrolytes and for a common initial concentration of 10 mg C-PAM/g PCC.

All the results illustrate that the C-PAM amount adsorbed increases gradually until reaching the equilibrium.

Analysing Figures 3 and 4, it is obvious that the molecular size of the polyelectrolyte is an important parameter influencing the adsorption kinetics. Adsorption was faster with the E1 series (Figure 3 (a) and (b) and Figure 4), this meaning that equilibrium was reached, in this case, for a lower contact time. That is, the time to achieve saturation of particle surface was lower. Moreover, for a similar architecture, the amount of polyelectrolyte adsorbed is higher for the E1 series (see Figure 4 and compare Figure 3 (a) and (b) with Figure 3 (c) and (d)). This is due to the differences of the adsorbed polyelectrolyte conformation on the particle surface. Lower molar mass polyelectrolytes adsorb with a flatter conformation and, thus, each molecule occupies a larger region of the particle surface for equal charge density. This is indicative of a change on the adsorption and flocculation mechanism, from bridging to bare patch, when the molar mass decreases (Gregory, 1988, Bajpai and Bajpai, 1995 and Gregory and Barany, 2011). Of course, once the polyelectrolyte starts adsorbing in patches, lowering the molar mass still further can eventually lead to the need for larger amounts of polyelectrolyte for full surface coverage.

The comparison between E1 and E1++++ shows that E1++++ reaches the equilibrium faster (see Figure 4 and Figure 3 (a) and (b)). The same happens if we compare the adsorption curves for E2 and E2++++ (Figure 4 and Figure 3 (c) and (d)). In this latter case the effect of branching on the time required to reach equilibrium is even more notorious, because the introduction of branches in the polyelectrolyte molecule must have led to a change in the flocculation mechanism from patching (when using the linear polymer E2) to bridging (when using the branched E2++++), as will be discussed below in section 3.4.

The effect of the polyelectrolyte charge density on the adsorption kinetics can be evaluated by analysing Figure 4 and comparing Figure 3 (a) and (b) with Figure 3 (e) and (f). When the charge density is higher, equilibrium is reached for a lower contact time. For instance, comparing the results for the two linear polyelectrolytes E1 and F1 (Figure 3 (a) and (e)), for 16 min of contact time we are already close to the equilibrium in the case of E1 but far from that in the case of F1 with a lower charge density (see Table 2). This was to be expected since adsorption is favoured when the charge density increases.

Comparing the results obtained for F1 and F1++++ (Figure 4 and Figure 3 (e) and (f)), with similar architecture to the E1 series but with a lower charge density, it is observed again that the branched polyelectrolyte reaches the equilibrium slightly faster.

The amount of polyelectrolyte adsorbed at equilibrium is slightly higher for F1 than for E1, which must be related with the more extended conformation of the less charged polyelectrolyte.

3.3. Langmuir isotherm fit

The Langmuir theory can be used if the sorption takes place at specific homogenous sites in the adsorbent. This theory is valid for monolayer adsorption, when the adsorbent is homogenous (binding sites homogeneously distributed on the particles surface) and surface and bulk phases exhibit an ideal behaviour. The Langmuir adsorption isotherm is described by the following equation (Langmuir, 1918, Tekin et al., 2005, Deng et al., 2006 and Greluk and Hubicki, 2009):

$$\frac{C_e}{Q_e} = \frac{1}{Q_m \times K} + \frac{C_e}{Q_m} \qquad (4)$$

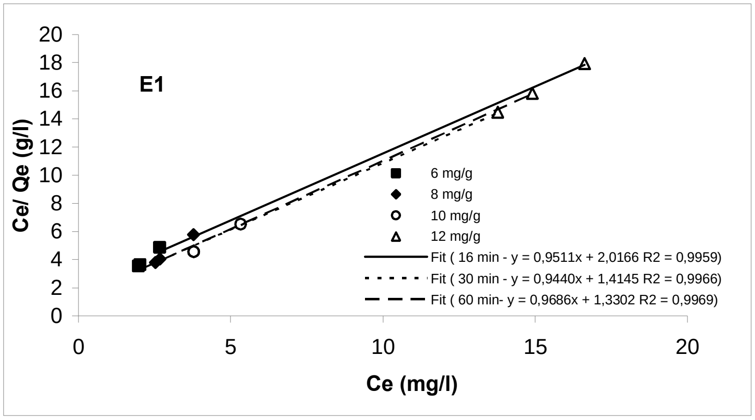
Where Q_m (mg/g) is the maximum amount of C-PAM per unit weight of precipitated calcium carbonate to form a complete monolayer coverage on the surface, C_e the equilibrium C-PAM concentration, and K is the Langmuir constant related to the affinity to binding sites (L/mg) (Hernandez Barajas et al., 2001). Higher K values correspond to a stronger affinity polyelectrolyte/particle.

The Langmuir model defines a dimensionless separation factor, R_L, related to the adsorption kinetics, which is defined as (Tekin et al., 2005):

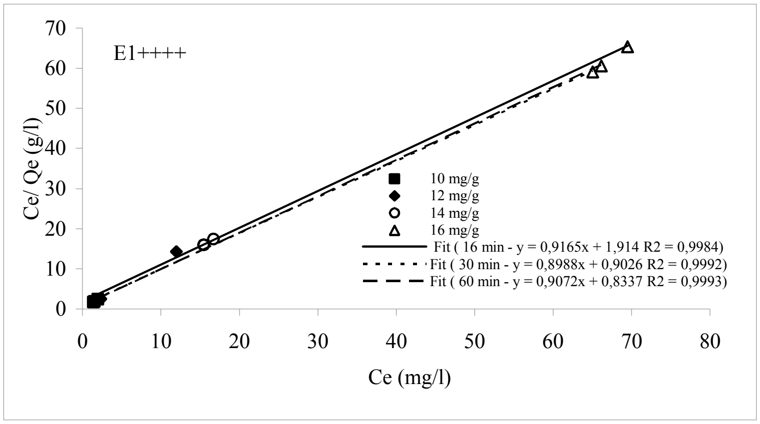
$$R_L = \frac{1}{1 + K \times C_e} \tag{5}$$

The value of R_L gives information about the type of adsorption prevailing, indicating the shape of the isotherm: if unfavourable adsorption exists $R_L > 1$, for $R_L = 1$ the isotherm is linear while adsorption is favourable for $0<R_L< 1$. With $R_L = 0$ adsorption is irreversible (Tekin et al., 2005 and Gregory and Barany, 2011).

Figure 5 presents three examples of the Langmuir isotherm linear regression fit for the polymers E1, E1++++ and E2. A linear fit was always obtained for all the polyelectrolytes tested, over the entire concentration range studied, with a good correlation coefficient (usually around 0.99). The fact that the Langmuir isotherm fits the experimental data is a confirmation of the monolayer coverage of C-PAM onto the PCC (Burchard, 1999).



(a)



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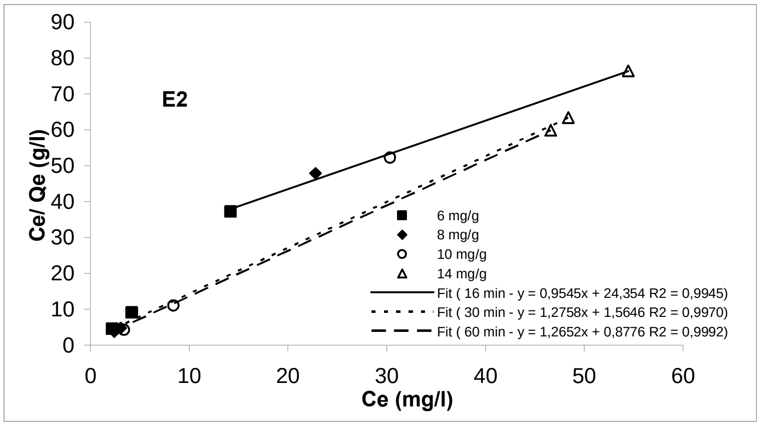


(c)

Figure 5**. Langmuir adsorption isotherm fit for E1, E1++++ and E2.**

From the Langmuir isotherms linear regression fit we have calculated the maximum amount of C- PAM adsorbed for monolayer coverage and the Langmuir constant, K. R_L was calculated for the low and high equilibrium concentrations measured. The information obtained from the Langmuir isotherms is summarized in Table 3. In this table, information is supplied only for the contact time, which enabled, for each polyelectrolyte, reaching the equilibrium (no more adsorption occurred).

Table 3. Summary of the Langmuir isotherm fit parameters.

Copolymer	Contact time (min)	Q_m (mg/g)	K (L/mg)	R^2	R_L (low-high concentration)
E1	30	0.71	1.50	0.9966	0.2531-0.2230
E1++++	16	0.52	2.09	0.9984	0.1969-0.0681
E2	60	0.64	1.23	0.9970	0.1626-0.1128
E2++++	60	0.61	1.46	0.9956	0.9193-0.0136
F1	30	0.49	1.90	0.9960	0.1856-0.0770
F1++++	30	1.28	1.17	0.9999	0.3675-0.1078

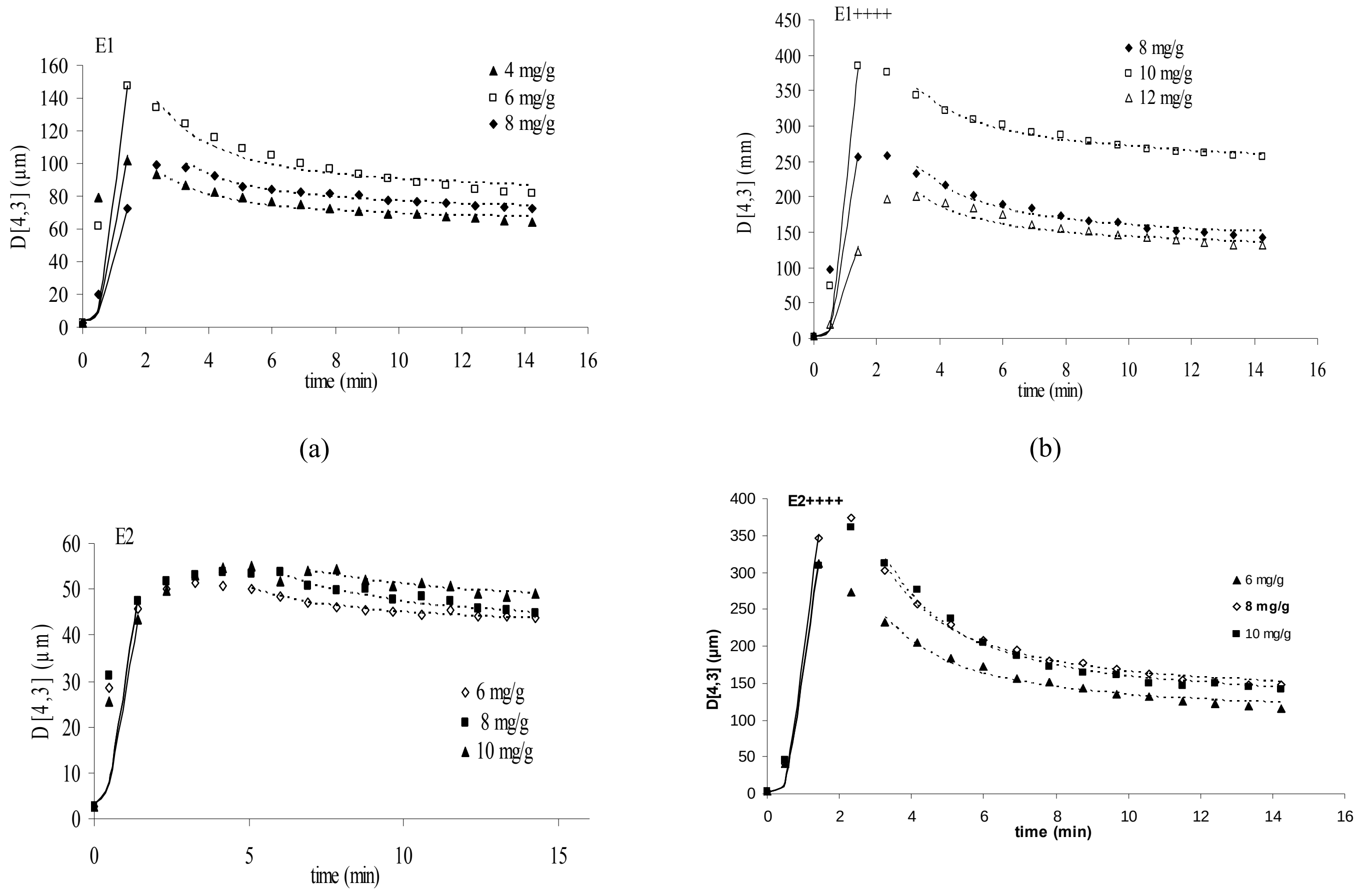
Comparing the values of K obtained at the equilibrium time, the polyelectrolytes with stronger affinity to the precipitated calcium carbonate particles are E1++++> F1> E1> E2++++, while E2 and F1++++ show the lowest K values. When the affinity is stronger, a lower maximum amount of polyelectrolyte is required for surface coverage (see Table 3). Also, for the polyelectrolytes with higher affinity coefficient, the equilibrium was always reached for a lower contact time. In general, higher molar mass and a higher degree of branching led to a higher value of the affinity parameter. Contrary to what was to be expected, F1 shows a very high affinity to the particles, when compared, for instance, with E1 (higher charge density) and F1++++, probably due to its higher molar mass (see Table 2).

The value of R_L varied between (0.0136–0.9193) indicating that the adsorption process was always favourable. For the higher concentrations R_L approached zero, indicating that adsorption had become irreversible, as expected for higher concentrations.

3.4. *Correlation between adsorption and flocculation kinetics*

Figure 6 provides four examples of the flocculation kinetic curves obtained by Laser Diffraction Spectroscopy (E1, E1++++, E2 and E2++++). The different trend in the kinetic curves becomes obvious when comparing the results for E1 and E1++++ (higher molar mass) with the result for E2, or still the results for E2 and E2++++. For the first two polymers the floc size reaches a maximum and then decreases till it stabilizes, due to aggregates restructuring and polyelectrolyte reconformation on the particle surfaces. This is typical of the bridging mechanism. For E2, no aggregate restructuring could be found. This is indicative of a change in the flocculation mechanism when the polyelectrolyte molar mass decreases, for the same charge density of the polymer (medium charge density). For E1 and E1++++, bridging is the predominant flocculation mechanism, while for E2 bare patch flocculation must be the main mechanism (Rasteiro et al., 2008 and Rasteiro et al., 2011). When branches are introduced in the polyelectrolyte chain, bridging assumes again importance. This change of mechanism is also obvious when we analyse the differences in the structure of the flocs resulting from the use of the different polyelectrolytes, as will be discussed below (see Table 4). In

Figure 6, the fit of Equations (1) and (2) to the experimental kinetic curves is also presented (solid and dashed lines, respectively). This fit was always good.



(a)

(b)

(c)

(d)

Figure 6. Flocculation kinetic curves for E1, E1++++, E2 and E2++++ showing the experimental data points and the fits of Eq. (1) - solid lines and Eq. (2) – dashed lines.

Table 4 provides the comparison of the results from the adsorption tests (amount of polyelectrolyte adsorbed at equilibrium (Q_e)) and from the flocculation tests (kinetic constant (k_1) for the first stage of flocculation according to Figure 1 and the maximum floc size reached at the end of this stage). In this table also the values of the scattering exponent (SE) for the maximum in the flocculation kinetics curve are included. They were calculated from the scattering matrix obtained by Laser Diffraction Spectroscopy (Biggs et al., 2000), and are related to the structure of the secondary aggregates (Biggs et al., 2000 and Rasteiro et al., 2011). Higher scattering exponent values mean more compact aggregates. The flocculation data presented in Table 4 is for the optimum flocculant concentration, defined as the one leading to larger flocs and fastest kinetics (Rasteiro et al., 2008). The optimum flocculant concentration is also indicated in that table.

The adsorption results for the E1 series show that adsorption is slower for the case of E1 (lower Q_e value and higher contact time to reach the equilibrium) than for E1++++. Flocculation is also slower for E1 and faster for E1++++, if the first stage of flocculation is considered (see the values of k_1). The same trend exists when comparing adsorption and flocculation rates for E2 and E2++++ and for F1 and F1++++.

Copolymer	Contact time (min)	Q_e (mg/g)	Optimum flocculant concentration (mg/g)	k_1 (min^{-1})	k_2 (min^{-1})	$d_{50, max}$ (μm)	SE
E1	30	0.9513	6	2.76	0.73	134	2.07
E1++++	16	1.0632	10	3.50	0.79	298	1.39
E2	60	0.7785	8	2.02	0.56	50	2.19
E2++++	60	0.8966	8	3.48	0.33	331	1.68
F1	30	0.9015	8	2.69	0.63	109	2.25
F1++++	30	1.1440	10	3.51	1.23	327	1.39

Table 4. Comparison of the results from the adsorption and flocculation kinetics**.**

Comparing E1 and E2 to evaluate the influence of molar mass on the flocculation mechanism, both the adsorption rate and flocculation rate (as determined by the kinetic constant k_1 in Table 4) are lower for E2. If we compare E1++++ and E2++++, again, both the adsorption and flocculation rates are lower for E2++++ (lower molar mass). So, lower molar mass has a detrimental effect on both the adsorption and aggregation stages, but this influence is not so determinant when branches are introduced in the molecule.

Looking now at the values of scattering exponent values at the end of the first stage of flocculation, low adsorption rate leads to lower flocculation rate and to more compact flocs (higher scattering exponent values). Moreover, the linear polyelectrolytes give smaller and more compact flocs at the end of the first stage of the flocculation process, dominated by aggregation, while the highly branched polymers lead to higher adsorption rates and, thereafter, faster flocculation rates for this stage, producing, as a consequence, more open flocs (lower SE values). This confirms the predominance of the bridging mechanism for the higher molar mass polyelectrolytes once branches are introduced in the chains, which result in more open flocs, in opposition to what happens for the lower molar mass polyelectrolytes, which lead to more compact flocs as a consequence of the predominance of the patching mechanism.

The amount of polyelectrolyte adsorbed at equilibrium is higher for the E1 series than for the E2 series. This confirms again the influence of the molar mass on the flocculation mechanism when changing from a very high molar mass polyelectrolyte to a medium molar mass, for the same charge density. Higher molar mass polyelectrolytes act according to the bridging mechanism, and, despite the larger dimension of the molecule, coverage achieved by each molecule can be lower and, thus, higher polyelectrolyte amounts are required to reach the equilibrium, in opposition with what happens for medium molar mass polyelectrolytes, which act according to the patching mechanism.

4. Conclusions

Cationic polyelectrolytes (C-PAM), varying in molar mass, charge density and chain architecture were tested in terms of adsorption on precipitated calcium carbonate and the performance in flocculation. The tests further included the influence of the polyelectrolyte characteristics on the flocs size and structure.

Overall it can be concluded that a low adsorption rate leads to lower flocculation rate and, usually, to more compact flocs. Typically, a lower adsorption rate is identified with the patching mechanism, while faster adsorption corresponds to the bridging mechanism.

The adsorption results show that for polyelectrolytes of similar molar mass, highly branched polyelectrolytes reach the equilibrium faster than linear polyelectrolytes. Similarly, the flocculation rate is faster for the branched polyelectrolytes. This tendency was observed consistently for series of polyelectrolytes of various molar mass and charge density. Regarding the effect of molar mass, lower molar mass leads to lower adsorption rates and, simultaneously, slower flocculation.

The Langmuir isotherm model described well the experimental adsorption isotherms. From the fit of this model, the amount of adsorbed polymer required for monolayer coverage could be extracted. When this value increases, the flocs obtained are usually more compact and smaller. Moreover, this can also be correlated with the affinity of the polyelectrolyte to the precipitated calcium carbonate particles. Polyelectrolytes with stronger affinity to the particles require a smaller amount for monolayer coverage and lead to faster adsorption and higher flocculation rates, the flocs being more open.

Acknowledgments

The authors thank FCT (Fundação para a Ciência e Tecnologia, Portugal) contract PTDC/EQU-EQU/66669/2006 and Pest-C/EQB/UI0102/2013 and the Swiss National Science Foundation (grants 200020_119818 and 200020_135162) for the financial support, AQUA+TECH Specialties SA (La Plaine, Geneve, Switzerland) for supplying the flocculants samples and OMYA for supplying the precipitated calcium carbonate samples.

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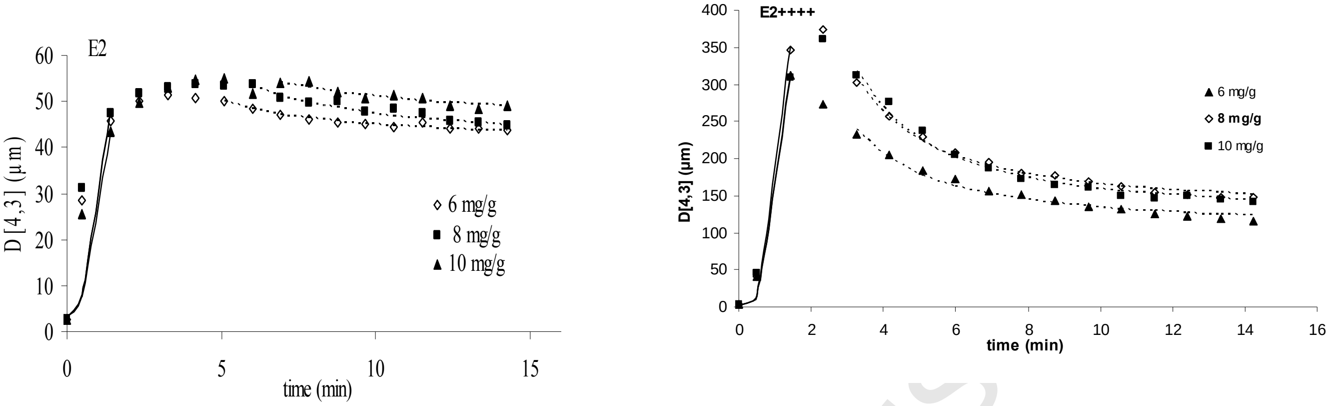
List of figures

List of tables



Influence of branches in the polymer chain on flocculation kinetic curves (comparison between E2 and E2++++)