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Flocculation treatment of an industrial effluent: performance assessment by Laser Diffraction Spectroscopy

Anita Lourenço[1,2], Julien Arnold[2], Olivier J. Cayre[3] and Maria G. Rasteiro[1]*

[1] Chemical Engineering Department, CIEPQPF, University of Coimbra Pólo II, Rua Sílvio Lima, 3030-790 Coimbra, Portugal

[2] Aqua+Tech Specialities SA, Chemin du Chalet-du-Bac 4, 1237 Avully, Geneva, Switzerland

[3] School of Chemical and Process Engineering, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, UK

*mgr@eq.uc.pt

ABSTRACT

Flocculation processes are extensively used as separation method to remove suspended and dissolved solids, colloids and organic substances in effluents. As flocculation performance affects the economy of many industrial processes, it is important to understand the underlying mechanisms, as well as the predominant flocculant properties influencing the final results. In the present study, a strategy based on the use of laser diffraction spectroscopy (LDS) was developed to screen different flocculants performance in an industrial potato crisopmizps manufacturing effluent, using anionic polyelectrolytes as flocculants. The flocculation process was monitored over time and information on floc average size and structure was obtained. The effect of flocculants properties, including their hydrophobic content, and concentration on the flocculation process and on flocs density was investigated. With this methodology for continuous monitoring of the flocculation process in real effluents, it is possible to obtain simultaneously information about the kinetics of floc size evolution, and also about the evolution of floc structure with time. This is an important proof of concept, since it will allow, in the future, to perform pre-screening of polymers to be used in the flocculation treatment of a specific effluent, minimizing, in this way, pilot trials. The highest polyelectrolyte concentration studied leads to the largest flocs obtained, which were, however, very sensitive to the turbulent environment. This agrees with the low scattering exponent values obtained for all the flocs, which indicate an open and porous floc structure. Characteristics of the polymers used proved to have an important role in the floc size. Higher zeta potential, hydrodynamic diameter and molecular weight of the flocculant resulted in larger flocs. The presence of hydrophobicity in the polyelectrolyte also showed to influence the floc properties, although an optimum content could be identified, above which flocculation was hindered.

KEYWORDS

Polyelectrolytes, wastewater treatment, flocculation, laser diffraction spectroscopy, scattering exponent.

INTRODUCTION

Wastewater from industrial processes usually contains dissolved solids, very fine suspended solids, organic and inorganic particles, metals and other insoluble impurities with very small size and some surface charge. Due to this, self-aggregation of these particles in a way that it is possible to have a reasonable separation and obtain dense flocs for settling and filtration is a challenge[1,2].

Flocculation is the most extensively used separation process to remove suspended and dissolved solids, colloids and organic substances in industrial wastewater[3]. Generally, floc formation involves several steps occurring sequentially including dispersion of the flocculant in the solution, diffusion near and to the solid-liquid interface, adsorption of the flocculant onto the surface of the particles, collision of particles containing adsorbed polymer with other particles and adsorption of the flocculant on the free surface of those particles. These standard steps typically lead to the formation of aggregates and enable growth of initial microflocs to larger and stronger flocs by consecutive polymer adsorption and particle collisions and aggregation or, alternatively, establishment of bonds between flocculant chains absorbed onto different particles[4–6].

Destabilization of particle suspensions by polymers can be associated to different flocculation mechanisms such as charge neutralization[6,7], polymer bridging[8,9] and electrostatic patches interactions[9,10]. These mechanisms are strongly related with the way adsorption of flocculants on particle surfaces occurs, which depends on the chemical affinity between the polymer and the particle surface[3].

To optimize the flocculation performance there are several parameters that need to be controlled during the process. The optimized flocculant concentration depends on the content of suspended solids and colloids in the wastewater, including dissolved organic content, and the treatment success usually increases with the increase of flocculant input, until a certain optimum level from which there is no further improvement of performance. The treatment efficiency often achieves a maximum and decreases if the polymer dosage is too high[11]. An important mechanical factor in the flocculation process is the mixing, which enhances contact between the flocculant and the suspended solids in the system, thus accelerating the formation of flocs. There are two stages in the mixing process in a typical flocculation process and they are associated with rapid and slow stirring. The rapid stirring is used to achieve a good dispersion of the flocculant after addition, while slow stirring is used to promote the flocs growth and limit the breakup of aggregates[12].

Synthetic polyelectrolytes have been commonly used as flocculants to enhance the flocculation process efficiency, with promising results[13]. Polymer characteristics such as molecular weight, structure (linear or branched), charge density, charge type and composition have a strong influence on the flocculation process[14].

In order to investigate the floc behavior during the formation process, as well as the flocculation kinetics, the floc characteristics can be monitored in-situ using a laser diffraction particle size analyzer system (LDS)[15]. It is well reported in the literature that LDS is useful to follow flocculation processes, even if most studies refer to model systems[15]. Rasteiro *et al.*[15,16] presented the application of LDS to monitor flocculation in papermaking and to evaluate the flocculation mechanisms in flocculation studies of precipitated calcium carbonate. Using LDS it is possible to perform an evaluation of the flocculants performance, providing information on floc size distribution, average size and aggregate structure described by the fractal dimension (d_F) and scattering exponent (SE), in a continuous approach[17]. The fractal dimension provides information about the primary particles that fill the space in the nominal volume of an aggregate, being a useful parameter to characterize the density of the flocs[18]. However, for secondary aggregates resulting from the aggregation of primary aggregates, the fractal theory can no longer be applied and the scattering exponent is used to obtain information regarding the flocs structure, providing information for the larger length scales of larger flocs[17,19]. Moreover, flocculation can be conducted in controlled hydrodynamic conditions that can easily be reproduced in industrial flocculation processes[20].

In LDS measuremnt, the scattering angle, the angle between the incident and scattered lights, is inversely correlated with the particles size. Thus, by collecting the intensity of the scattered light for different angles it is possible to extract information about the number of particles in each size class. The information collected regarding the different scattering angles, results in the scattering matrix, from which the particle size distribution can be obtained using the adequate model[21].

In this study, flocculation was followed continuously, using LDS, for a real industrial effluent from potato crisps manufacturing industry, treated with high molecular weight anionic polyelectrolytes with two different polymer compositions (co-polymers). The effect of the incorporation of a hydrophobic monomer at different ratios (ter-polymers) within the polymer flocculant structure, onto the efficiency of the flocculation process was also studied. Recently, hydrophobic modification of polymers has been extensively investigated for application in solid-liquid separation, due to their capacity of enhancing polymer performance[22]. Hydrophobically modified polymers can be obtained by chemical grafting or copolymerization procedures, through the introduction of a relatively low amount of hydrophobic monomer into the polymer structure[23]. The synergetic effects between the charge functionality and the hydrophobic group have shown a remarkable improve of performance in wastewater treatment[22,24].

In this study the applied polymers were synthesized by inverse-emulsion polymerization using three different health-friendly formulations, which have replaced the organic phase and surfactants of traditional formulations[25]. Two health-friendly oils, according to the international nomenclature of cosmetic ingredients INCI, were used as organic phase in the synthesis process: an iso-paraffin (Carnation) and a hydrogenated polydecene (Puresyn4). These health-friendly formulations, which have been explained in a previous reference from the authors[26], have already proved to be suitable to synthesize standard commercial polymers for application as flocculants in water treatment. Results regarding size, structure and strength of the flocs, as well as flocculation kinetics were obtained and analyzed. Correlation between polyelectrolyte characteristics and flocs size and structure is presented here and the prevailing flocculation mechanisms discussed. The main objective of this work is the development of a new screening methodology, based on LDS, to pre-select the best flocculant for a specific application. This will allow the detailed analysis of the obtained aggregates, depending on the flocculation products used and operating conditions, and allow correlating polyelectrolyte characteristics with specific floc properties, thus facilitating the choice of the best polyelectrolyte for a certain application, minimizing the need for pilot trials.

EXPERIMENTAL SECTION

Materials

Acrylamide (AAm) solution, at 50 wt %, was purchased from Kemira (Botlek, Netherlands). The monomer Acrylamido-2-methyl-1-propanesulfonic acid sodium salt solution (Na-AMPS), at 50 wt%, was purchased from Lubrizol (Bradford, UK) and used as received. Ethyl acrylate (EA) was purchased from Evonik (Darmstadt, Germany). Tert-butyl hydroperoxide (TBHP) was purchased from Acros Organics (Geel, Belgium). Sodium meta bisulfite (MBS) was purchased from Brenntag (Esseco, Italy). Adipic acid was purchased from Merck (Hohenbrunn, Germany). The surfactants Sorbitan isostearate (Crill 6) and Synperonic LF/30 were purchased from Croda (Goole, England). PEG-7 hydrogenated castor oil (Cremophor WO7) was purchased from BASF (Ludwigshafen, Germany). The oil Puresyn4, a hydrogenated polydecene, was purchased from ExxonMobil (Switzerland). Carnation, an iso-paraffin, was purchased from Sonneborn (Amsterdam, Netherlands). PPVS and methylene blue were supplied by Sigma-Aldrich (St. Louis, USA). Sodium Chloride (NaCl) was purchased from VWR (Leuven, Belgium).

The flocculation tests were carried out on an industrial oily effluent from potato crisps manufacturing industry, which was supplied by Adventech Group (Portugal). The initial effluent sample presented a pH of 12.8, COD of 21.6 gO_2/L, total solids of 9.7 g/L and a turbidity of 3050 NTU. The zeta potential of the effluent was measured in a Zetasizer Nano-ZS (Malvern Instruments) and the average value obtained was −17 mV at the initial pH (12.8) and -5 mV at pH 6, even if a wide distribution of zeta potential was obtained, indicative of particles with different charges. Considering that a few particles in the effluent were over 100 µm (being the maximum particle size recommended for this equipment 100 µm) and also the low zeta potential of the effluent particles, the number of runs for each measurement was increased, as well as the acquisition time, according to recommendations in the equipment manual. The software quality report did always confirm good quality of the measurements.

Polyelectrolytes synthesis

Anionic polyelectrolytes, co- and ter-polymers of acrylamide, Na-AMPS and ethyl acrylate, were synthesized by inverse-emulsion polymerization using health-friendly formulations. The polymerization was carried out in a 500 mL glass reactor. Prior to reaction, the aqueous phase was prepared with deionized water, acrylamide, Na-AMPS and with 0.625 wt % of adipic acid. Sorbitan isostearate and PEG-7 hydrogenated castor oil were, as well, the surfactants blend to obtain a hydrophilic–lipophilic balance (HLB) between 4.75 and 5.75, adapted to the monomers composition and organic phase used. Carnation and Puresyn4 were used as organic phases. The aqueous phase was added to the organic phase under mechanical stirring and in the case of the combination with the hydrophobic monomer, the desired amount of EA was added at this point to the emulsion. TBHP and sodium MBS were used as the initiator redox couple. After the batch had cooled down to 32 ºC, 2.20 wt% of a wetting agent (Synperonic LF/30) was added.

Table 1 presents a summary of the flocculants produced. Lower anionic fraction is represented as the 50 series, while higher anionic fraction is represented as the 80 series. MC and MP series in the list correspond to the use of Carnation and Puresyn4, respectively, as the health-friendly synthesis organic phase. For the ter-polymers, only Carnation was used as organic phase. A, refers to the use of Na-AMPS monomer, while E refers to the introduction in the polymer of the hydrophobic monomer EA.

Polyelectrolytes solutions were prepared with distilled water at 0.4% (w/w). In order to guarantee the effectiveness of the flocculants, the diluted solutions must be prepared every day.

Table 1 Summary of the polyelectrolytes composition. Co-polymers: 50AC, 80AC, 50AP and 80AP. Ter-polymers: 50A1EC, 50A3EC, 80A1EC, 80A3EC.

Polymer designation	AAm ratio		Na-AMPS ratio		EA ratio		Synthesis organic phase
	(wt%)	(mol%)	(wt%)	(mol%)	(wt%)	(mol%)	
50AC	50.0	74.0	50.0	26.0	-	-	Carnation
80AC	20.0	42.0	80.0	58.0	-	-	Carnation
50AP	50.0	74.0	50.0	26.0	-	-	Puresyn4
80AP	20.0	42.0	80.0	58.0	-	-	Puresyn4
50A1EC	49.4	74.0	49.4	25.0	1.2	1.0	Carnation
50A3EC	48.5	72.0	48.5	25.0	3.0	3.0	Carnation
80A1EC	19.7	42.0	79.7	57.0	0.6	1.0	Carnation
80A3EC	19.0	40.0	79.0	57.0	2.0	3.0	Carnation

Polyelectrolytes characterization

All polymers were isolated using hexane, acetone and isopropanol, and the characterization experiments performed in samples in the dry powder state.

Charge density was determined by elemental analysis using an element analyzer EA 1108 CHNS-O (Fisons) and 2,5-Bis(5-tert-butyl-benzoxazol-2-yl) thiophene as standard. C, H and N elemental analyses were performed and the N element was used in the calculation of the charged fraction. At least three measurements for each sample were performed.

Hydrodynamic diameter, molecular weight and zeta potential of isolated and redissolved polymers were determined by dynamic light scattering (DLS), static light scattering (SLS) and electrophoretic light scattering (ELS), respectively, in a Malvern Zetasizer Nano ZS, model ZEN3600 (Malvern Instruments Ltd, UK).

For the hydrodynamic diameter, stock solutions of 0.05 g/L for copolymers and 0.03 g/L for terpolymers were prepared in Milli-Q water and stirred overnight. All samples were sonicated during 2 min and passed through 0.45 µm syringe filters prior to analysis. The measurement temperature was set to 25 ºC, backscatter detection (173º angle) was used and the CONTIN model was used to treat the signal, with at least three measurements for each sample performed.

Weight-average molecular weight measurements of polymers were performed using stock solutions (0.5 g/L) of each polymer prepared in NaCl 0.5 M and stirred overnight. The samples for analysis were then obtained by diluting the stock solutions at several concentrations from 0.5-0.02g/L. All samples were sonicated during 2 min and passed through 0.45 µm syringe filters prior to analysis. Toluene was used as standard. Previously, the refractive index of each solution was determined, in the refractometer Atago RX-5000D. By plotting refractive index versus concentration we could obtain *dn/dc* (variation of refractive index with concentration) which was supplied to the SLS software. The molecular weight value was extracted from the interception point on the X axis of the Debye plot, which represents the intensity of the scattered light versus the concentration of the sample used[27].

For zeta potential measurements, 1 mL of each stock solution (0.1 g/L) in Milli-Q water was carefully injected with a syringe into a folded capillary cell (ref. DTS1070), closed by cell stoppers. At least three measurements were conducted for each sample. Table 2 summarizes the flocculants characteristics.

Table 2 Summary of flocculants characteristics. Co-polymers: 50AC, 80AC, 50AP and 80AP. Ter-polymers: 50A1EC, 50A3EC, 80A1EC, 80A3EC.

Polymer designation	Charged fraction estimated from elemental analysis (wt%)	Zeta Potential (mV)	Hydrodynamic diameter (nm)	Weight-average molecular weight (10^6 Da)
50AC	41.5 ± 0.2	-71 ± 2	67 ± 2	0.9 ± 0.07
80AC	62.9 ± 0.5	-80 ± 1	72 ± 1	1.0 ± 0.08
50AP	41.9 ± 2.3	-72 ± 1	265 ± 37	2.5 ± 0.09
80AP	68.1 ± 2.1	-85 ± 1	147 ± 4	1.3 ± 0.2
50A1EC	39.5 ± 0.4	-65 ± 2	70 ± 1	0.6 ± 0.02
50A3EC	39.7 ± 1.2	-58 ± 1	282 ± 32	3.5 ± 0.07
80A1EC	62.2 ± 1.7	-79 ± 1	143 ±10	1.5 ± 0.2
80A3EC	61.6 ± 1.5	-79 ± 2	206 ± 22	2.4 ± 0.08

Flocculation jar tests

For each polymer developed, a 200-mL stock solution at a 0.4 wt% concentration was prepared with distilled water using magnetic stirring for sixty minutes. 75-mL samples of pre-agitated wastewater (industrial effluent) were adjusted to three different pHs using hydrochloric acid or sodium hydroxide aqueous solutions, using a pH meter SCAN3BW (Scansci). The pH values were chosen after a first pre-screening over all pH range. Polymer solution samples with different volumes were added to the wastewater sample, increasing successively the flocculant concentration from 13 mg/L until a maximum of 180 mg/L. In each addition, the suspension-polymer mixture was manually agitated for 10 seconds, allowed to settle for 2 min and the turbidity of the supernatant assessed, with at least three repetitions, using a Photometer MD600 (Lovibond, UK). The variance in the measurements of turbidity was always below 1.0 %.

Flocculation process monitoring

A 200-mL polymer stock solution at 0.4 wt% concentration was prepared with distilled water using magnetic stirring for sixty minutes.

LDS was used to monitor the flocculation process in slight turbulent conditions and supplies information about the flocculation kinetics and, simultaneously, on the alteration with time of the floc structure according to previous studies[15,20]. The tests were conducted in a Malvern Masterziser 2000 (Malvern Instruments). 200 mL of effluent sample were added to 600 mL of distilled water in the equipment beaker, and the pH was maintained at a value of 6 using hydrochloric acid, according to the turbidity reduction tests. Dilution was required to ensure an acceptable level of obscuration, which was initially below 80%, to guarantee that during the flocculation process, the end obscuration value was always above 5%, as suggested by Rasteiro *et al*.[15]. The measurements of the initial effluent, before any treatment, were carried out at a stirring speed of 2000 rpm. The flocculant was added after the first particle size acquisition of initial effluent at pH 6, as to obtain overall concentrations of the flocculant in the system of 3.3, 6.5 and 13 mg/L, according with the turbidity tests presented previously. Considering that, in the turbidity tests performed, the lowest concentration used (13 mg/L) conducted to very high turbidity reductions, sometimes to maximum reduction, thus, only this concentration and concentrations lower than this one were selected for the LDS monitoring experiments, in order to be able to observe considerable differences in floc sizes, and try to understand the presence of different and eventually complementary flocculation mechanisms. Moreover, economic considerations led also to the selection of a concentration of 13 mg/L as the basis concentration for the LDS tests. The predetermined amount of flocculant solution was added at once to the effluent. During the entire process, the flocculation vessel was stirred mechanically using the sample unit of the Malvern Mastersizer 2000 at a stirring speed of 300 rpm to avoid floc breakage but still ensuring that floc sedimentation was not occurring. Different stirring speeds were tested, from 200 to 900 rpm, however 300 rpm was found to be the optimized speed allowing the largest floc size while ensuring that flocs were successfully circulating in the system. The size of the flocs was measured every 36 sec for a period of 6.6 min. The reported values of the median particle size (d(0.5)) represent an average of at least three measurements.

Moreover, the scattering exponent of the flocs was calculated at the end of the flocculation process, from the scattering matrix obtained by LDS. This scattering exponent provides information about floc structure and is determined from the scattering pattern, corresponding to scattering at large length scales, considering that we are dealing with large and quite open aggregates[14]. From the scattering matrix obtained by the LDS, it is possible to plot, in logarithmic scale, the scattering intensity versus q, and the slope of the first region of the plot is related to the SE [17,19]. The q value is defined by the following equation (1):

$$q = \frac{4\pi n_0}{\lambda_0} \sin(\theta/2) \qquad \text{(Eq. 1)}$$

where n_0 is the refractive index of the dispersion medium, θ is the scattering angle and λ_0 is the incident light wavelength. The scattering matrix is exported through the Malvern software to an excel spreadsheet and the data is then processed, offline, for each acquisition, in order to obtain the scattering exponents.

RESULTS AND DISCUSSION

Flocculation jar tests

Results for turbidity removal with developed anionic flocculants at pH 3, 6 and 10 are presented in Figures 1 and 2. For this effluent, anionic co- and ter-polymers show very high turbidity reductions, with values above 97% at concentrations below 60 mg/L for the optimum pH (pH 6) and for polymers with lower anionic fraction (50 series). Since the removal results obtained for the co-polymers are already very high, the hydrophobically modified terpolymers did not lead to further improvements. In the case of the 50 series polyelectrolytes, the presence of the hydrophobic monomer seems not to affect much their performance, suggesting that this modification is not required for the achievement of good turbidity reductions, even if the kinetics of turbidity removal seems to be slightly faster in the case of the hydrophobically modified polymers (compare Figure 1 (a) with Figures 2 (a) and (c)). Looking at performances with the 80 series, there is a reduction of efficacy for the flocculant with a higher amount of the hydrophobic monomer, which leads to less turbidity reduction, indicating that a high amount of hydrophobicity is not beneficial for this specific case. This has already been observed by other authors previously[28].

The best performances were achieved with flocculants 50AC (97% turbidity reduction), 50AP (97% reduction), 50A1EC (97% reduction) and 50A3EC (97% reduction), in general, polymers with a higher molecular weight and medium charge density, which favors the bridging mechanism. Flocculation using polyelectrolytes with high molecular weight and medium charge density promotes the bridging effect, since the polymer chain adsorbs on the effluent particles surface and extends enough to interact with several particles. At pH 3 there is also significant turbidity removals for most of the polymers studied, however not as efficient as at pH 6 due to the initial destabilization of the particles observed at this specific pH, which leads to a very low absolute value of zeta potential. On the other hand, at pH 10 substantial reductions are only observed with the 80 series flocculants. Furthermore, for the co-polymers, a similar behavior was observed for polyelectrolytes developed with Carnation or Puresyn4 as organic phases, suggesting that the oil used in the synthesis formulation does not affect the flocculation performance.

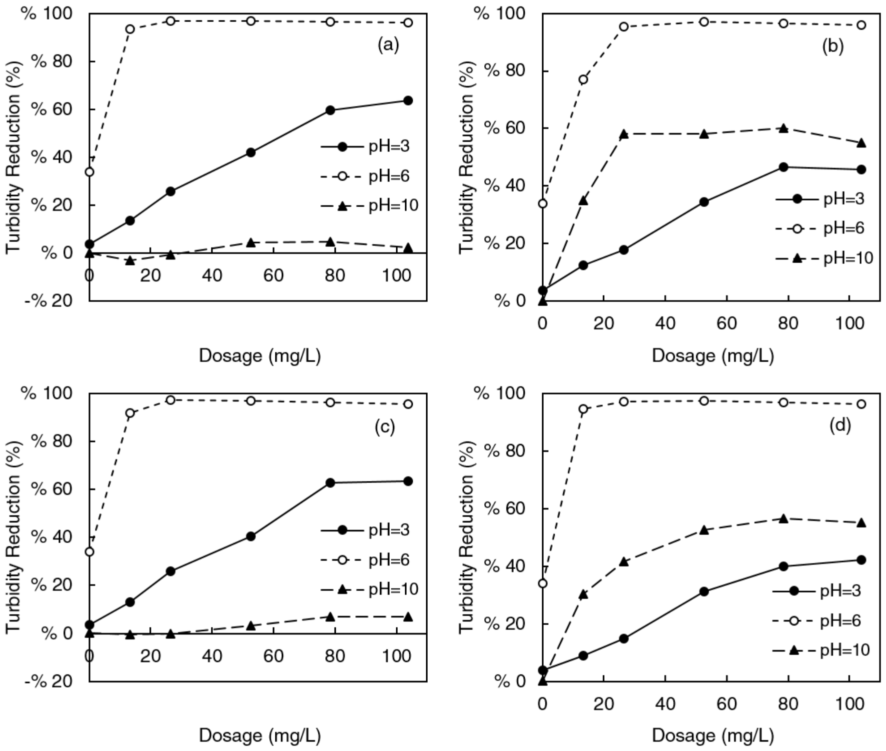

Figure 1 Turbidity removal curves for potato crisps manufacturing industry effluent treated by the anionic copolymers 50AC (a), 80AC (b), 50AP (c) and 80AP (d), at various pH.

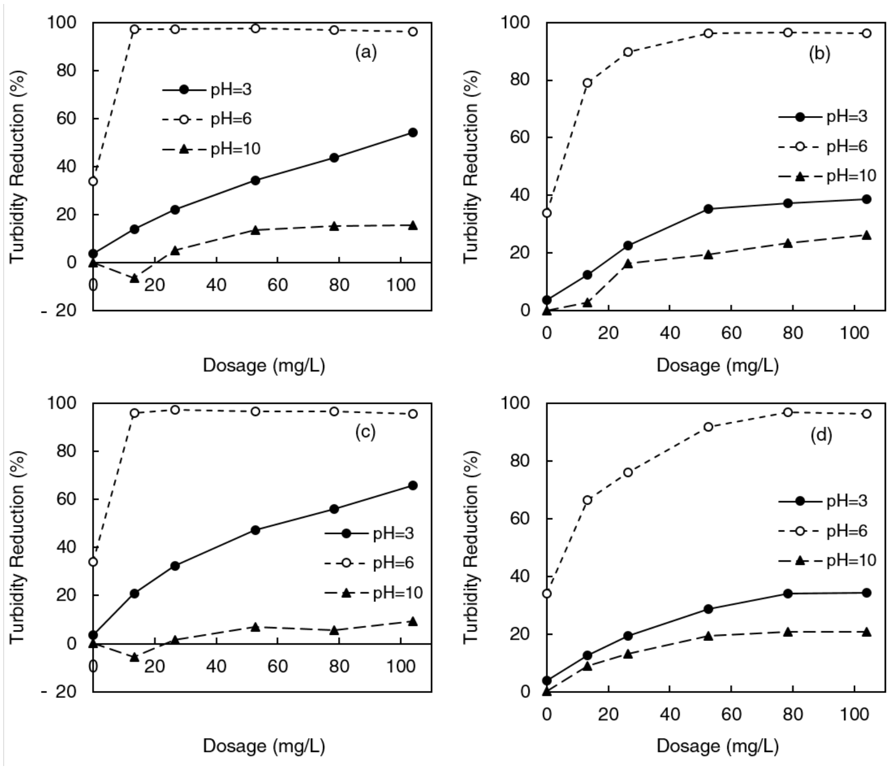

Figure 2 Turbidity removal curves for potato crisps manufacturing industry effluent treated by the anionic terpolymers 50A1EC (a), 80A1EC (b), 50A3EC (c) and 80A3EC (d), at various pH.

Flocculation process monitoring

Tables 1 and 2 present the composition and the results of the polyelectrolyte characterization. The composition measurements confirmed the targeted differences between polymers. This initial characterization subsequently allowed the separate study of each parameter influence (charge density and presence/absence of hydrophobic content) for polyelectrolytes with similar composition and architecture.

Zeta potential for initial effluent as collected (pH 12.8) and for effluent after adjustment to pH 6 (optimum pH for treatment, according with previous results) were measured and a decrease of the absolute value was observed (to -5mV) with the decrease of pH. Considering that this is an average value and the distribution curve goes between -20 mV and 15 mV, typical of a heterogeneous system as is the case of this real effluent, this means a large number of particles in the effluent have a positively charged surface, which justifies the success of anionic polyelectrolytes application. Anionic polyelectrolytes will attach to the positively charged particles of the effluent and the flocculation process must start from there, in a first stage, extending to the other particles through bridging and sweeping flocculation.

An example of the particle size distribution of the initial effluent, the pH 6 adjusted effluent and the effluent at the end of the flocculation process are shown in Figure 3, for treatment with ter-polymer 80A3EC. The particle size distribution evolves from a bimodal to monomodal distribution, being displaced towards higher particle sizes at the end of flocculation, as expected. The median size of the particles in the initial effluent, measured by LDS, was 39 μm, while after the pH adjustment it was 22 μm. This decrease of particle size is mainly due to the constant strong stirring speed applied during the measurement, until the polymer addition, which may cause breakage of existent small aggregates. Addition of flocculant increased drastically the median size of the particles. Specifically, adding the optimal dosage of 80A3EC (13mg/L) increased the median particle size to a value of 514 μm.

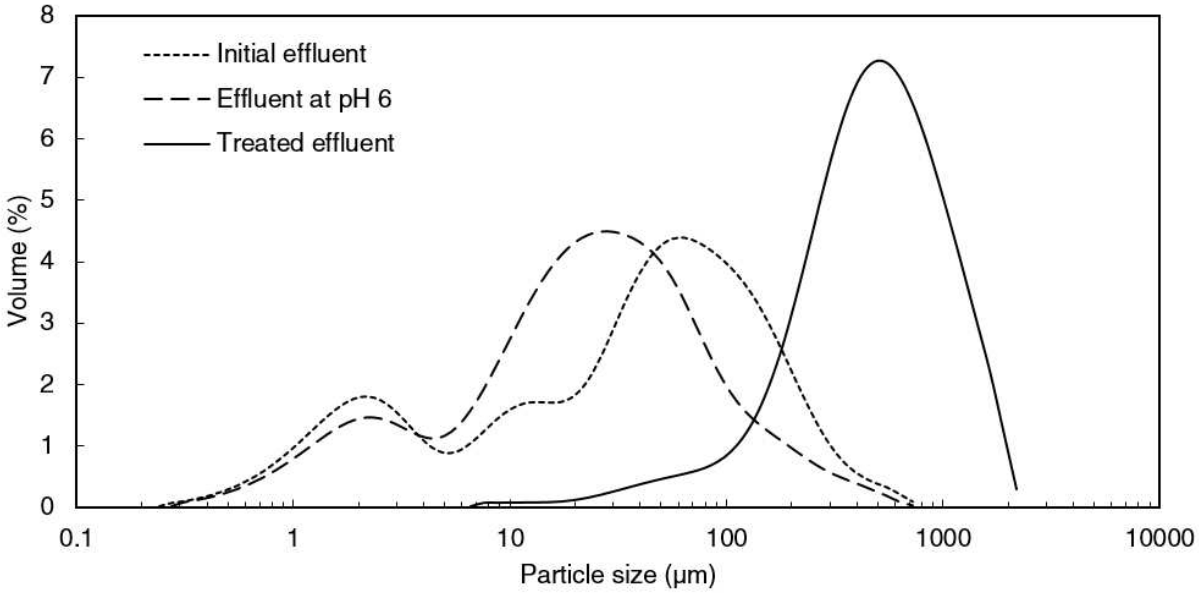

Figure 3 Particle size distribution of the initial effluent, pH 6 adjusted effluent and floc size distribution at the end of the flocculation with ter-polymer 80A3EC, for a polymer concentration of 13 mg/L.

Industrial effluent flocculation was monitored by measuring the aggregate size over time using the LDS technique. Figures 4 and 5 provide representation of flocculation kinetic curves obtained by LDS for the polymers tested (50AC, 80AC, 50AP, 80AP, 50A1EC, 50A3EC, 80A1EC and 80A3EC), for three different polymer concentrations (3.3, 6.5 and 13 mg/L). The trend in the kinetic curves is, in general, similar for all the cases tested. The average floc sizes reach their maximum within 2 min after polymer addition and then stabilize, without any apparent aggregate reconformation[17]. Analyzing the kinetic curves, and considering the instability of the flocs size over the time of flocculation, it is possible to conclude that flocs are considerably large and sensitive to the turbulent environment. The flocculant dosage for the polymers tested that led to larger flocs was always 13 mg/L, the highest concentration used in this study. Using lower concentration leads to a faster reach of the equilibrium point in some cases, but always resulting in smaller floc sizes.

Looking closer into the kinetic plots for the 13 mg/L concentration for the different polymers (Figure 4 and 5), it can be observed a floc size decrease after reaching a maximum size. This can be a result of the breakage of flocs by the hydrodynamic forces resulting from stirring, since the particles do appear to re-flocculate following breakage without visible restructuring, which, if present, would be noticeable through a steep decrease of flocs size, after reaching a maximum, in the median diameter curve versus time[20]. However, for lower concentrations of polymer, this behavior is less pronounced and the floc sizes are much more stable over time, confirming, as expected, that larger flocs are more sensitive to hydrodynamic forces resulting from mixing.

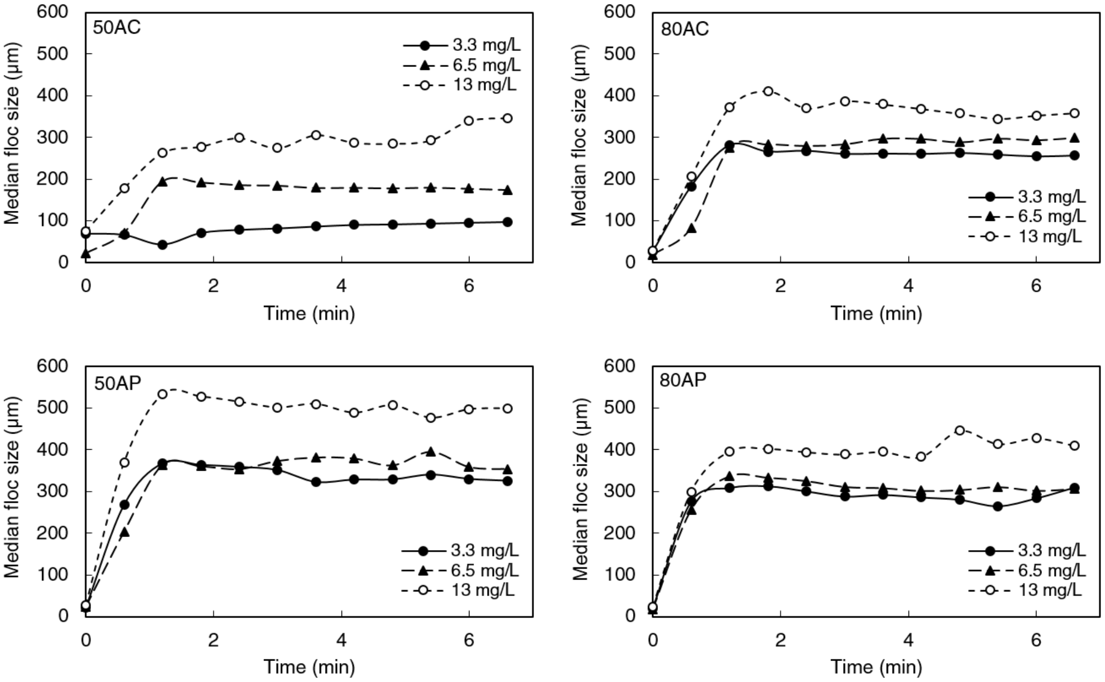

Figure 4 Evolution of average particle size over time obtained via LDS for three different flocculant dosages for co-polymers 50AC, 80AC, 50AP and 80AP.

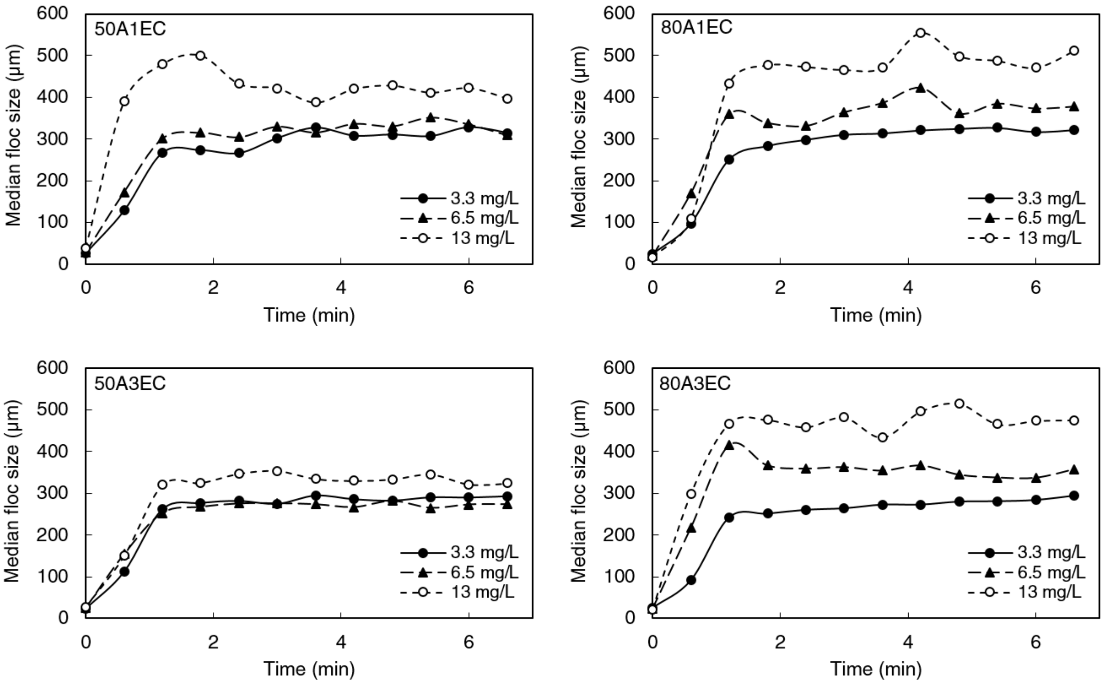

Figure 5 Evolution of average particle size over time obtained via LDS for three different flocculant dosages for ter-polymers 50A1EC, 50A3EC, 80A1EC and 80A3EC.

The SE profiles, calculated from the scattering matrix obtained by LDS, were plotted and the SE value after 6 min of flocculation, for each concentration and polymer, was extracted. These values are summarized in Table 3, alongside with particle sizes recorded 6 min after addition of the corresponding flocculant. Since the SE profiles for the different polymers follow all the same pattern, Figure 6 gives two examples of how SE evolves with time during the flocculation process, for two of the polyelectrolytes studied (80AC and 80A3EC), both with similar structure and charge, but differing by the ratio of hydrophobic monomer EA, used in the polymer synthesis. For all the cases, the scattering exponent increases rapidly at the beginning of the flocculation process, when a rapid growth of the floc size occurs. As the flocs grow, more particles are integrated within the flocs and the SE value increases correspondingly, until it eventually stabilizes within a few minutes. Higher SE values mean more compact flocs. Although it was not possible to obtain a value of SE for the initial effluent, due to the heterogeneity of the small size particles, a continuous increase of SE is still verified, revealing an increase of flocs compactness during flocculation, also due to the hydrodynamic forces. In general, and comparing with literature[20,29], where systems of calcium carbonate were used, values of SE for this specific effluent are lower, corresponding to more porous flocs. These results regarding floc structure suggest that the aggregation process takes place mainly by the bridging mechanism, supported by the fast flocculation rate and by the open floc structure. For these two polymers, a higher polymer concentration leads to more porous flocs. Additionally, the presence of the hydrophobic monomer within the polymer flocculant results in slightly more compact flocs.

The flocculation kinetics are largely dependent on the flocculant characteristics and on the flocculation mechanism involved [15]. Bridging is likely the main flocculation mechanism, since the polymers charge density varies between 25 and 58 mol% and, for lower charges, more extended conformation of the polymer chain is obtained on the effluent particles surface, due to the lower number of sites available for adsorption, leading to large and more open flocs. This is more evident by the analysis of the 50 series polyelectrolytes. The lowest values of SE (very open flocs), correspond to the larger flocs, and the opposite is also verified (Table 3). In general, introducing hydrophobic content in the polymer lead to larger and more porous flocs, suggesting an additional interaction promoted by the affinity between the oily effluent and the hydrophobic part of the polyelectrolytes. Comparing specifically 50A3EC and 80A3EC, which have similar hydrophobic content and different anionic fraction, it is possible to see higher SE values for 80A3EC, which means more compact flocs, compatible with the higher number of negative charges in the polymer chain. Additionally, flocs obtained with P series polymers (50AP and 80AP) are larger and more porous, in agreement with the higher molecular weight of these polymers.

Concerning the median floc size values (after 6 min) in Table 3, it is possible to see, for each polymer tested, an increase with the increase of the flocculant concentration, which was expected since more polymer in solution allows to create larger flocs by aggregating more particles. Also, comparing polyelectrolytes with the same characteristics of hydrophobicity, it is visible a tendency where larger flocs are obtained using flocculants with higher charge density (e.g. compare 50AC with 80AC or 50A1EC and

80A1EC). The exception is when comparing 50AP and 80AP, possible due to the much higher molecular weight of 50AP.

Table 3 Summary of the experimental value of SE after 6 minutes of flocculation for each polyelectrolyte and maximum floc size for each concentration tested.

Polymer	Concentration (mg/L)	SE after 6 min	Floc size after 6 min (μm)
50AC	3.3	1.81	95
	6.5	1.84	177
	13	1.69	340
80AC	3.3	1.68	254
	6.5	1.62	294
	13	1.58	352
50AP	3.3	1.53	330
	6.5	1.52	359
	13	1.39	497
80AP	3.3	1.52	283
	6.5	1.50	302
	13	1.44	428
50A1EC	3.3	1.37	328
	6.5	1.37	335
	13	1.35	423
50A3EC	3.3	1.46	290
	6.5	1.45	273
	13	1.43	322

80A1EC	3.3	1.60	317
	6.5	1.64	374
	13	1.46	471
80A3EC	3.3	1.73	284
	6.5	1.74	337
	13	1.65	474

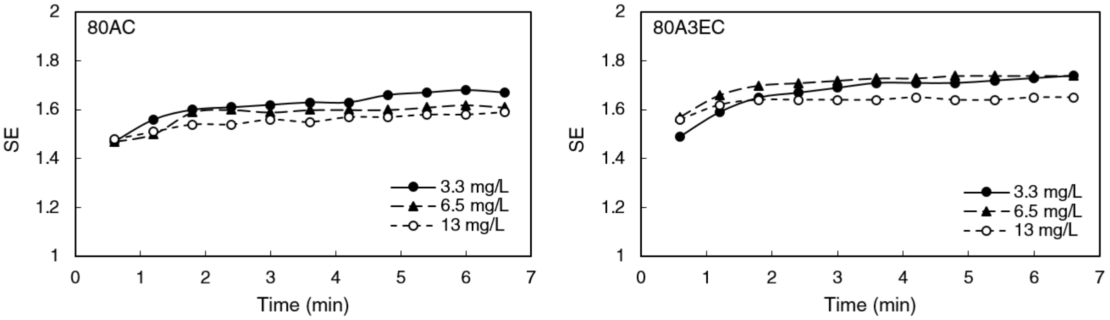

Figure 6 Evolution of floc structure (SE) for 80AC and 80A3EC, at different concentrations.

Correlating polymer characteristics with performance in flocculation

Figure 7 shows the influence on the floc size (Table 3) of charged fraction (a), zeta potential (b), hydrodynamic diameter (c) and molecular weight (d) of the polyelectrolytes, for the higher polyelectrolyte concentration used (13 mg/L). The results plotted refer to the flocs average size, in the average size over time curves, after 6 min of flocculation. In general, higher charged fraction and zeta potential, in absolute value, lead to larger flocs, since there is more charged moieties on the polymer, resulting in increased number of attachment events to particle surface per polymer chain, thus increasing the statistical possibility of one chain adsorbing to two or more particles, conducting to aggregates with a larger number of particles. This tendency is not completely linear, but for both co- and ter-polymers it can be verified in most of the cases, with only the exception of co-polymer 50AP (identified in the graph), which presents a molecular weight value much higher than the other co-polymers, introducing, thus, another parameter that can mask the trend. When considering the polymer hydrodynamic diameter, it is evident that the floc size increases when the hydrodynamic diameter increases, with the exception for the ter-polymer 50A3EC (identified in the graph), which appears as an outlier, for which a molecular weight value higher than for the other ter-polymers was also measured. However, the size distribution of this ter-polymer indicates the existence of some aggregation which may be masking the molecular weight measurement and even the hydrodynamic diameter measurement. Moreover, previous studies in the literature [28], have already referred to the possibility of an optimum amount of hydrophobic monomer incorporation in the polymer chain, above which flocculation is no longer improved, as will also be discussed here later. Since hydrodynamic diameter is very well correlated with molecular weight values, the tendency observed regarding the influence of hydrodynamic diameter is similar to the one observed in Figure 5 (d) for the influence of molecular weight. Longer polymer chains result in larger flocs, as one polymer chain can adsorb to the surface of a larger number of particles in the same floc, which, consequently, are usually also more porous. Moreover, the inclusion of the hydrophobic monomer usually leads to larger flocs as the result of two phenomena: higher affinity to the particles and higher molecular weight and hydrodynamic diameter (see Table 2).

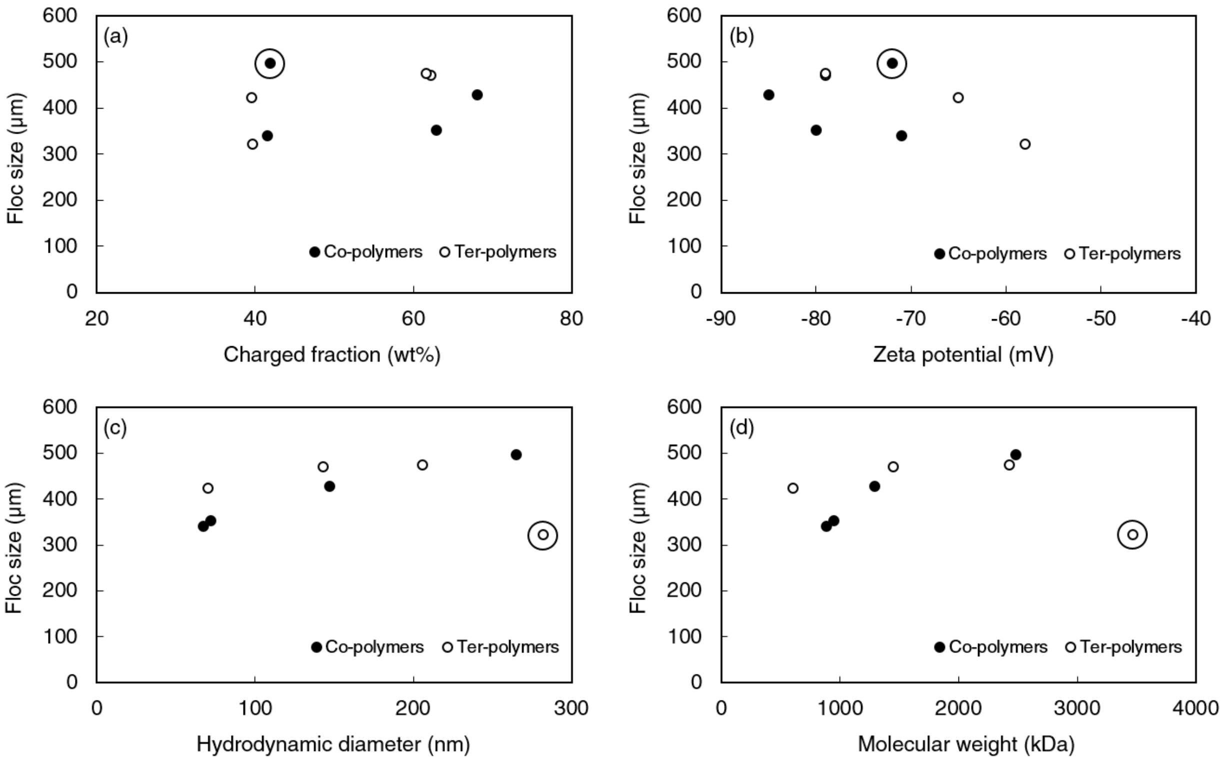

Figure 7 Floc size after 6 min as function of charged fraction (a), zeta potential (b), hydrodynamic diameter (c) and molecular weight (d) for the highest polyelectrolyte concentration tested (13 mg/L).

The influence of zeta potential (a) and hydrodynamic diameter (b) of the polyelectrolytes on scattering exponent (Table 3), for the higher polyelectrolyte concentration used (13 mg/L), is presented in Figure 8.

Polyelectrolytes with higher absolute values of zeta potential, corresponding to a higher charge density in the chain, are expected to form more compact flocs (higher SE values), since there are more regions in the polymer chain able to adsorb to the effluent particles. However, this is only observed in the case of the ter-polymers with a strong effect of charge density on the flocs structure. Co-polymers show almost no influence of charge density on the floc structure, perhaps due to the overall lower molecular weight of these polymers.

Regarding influence of hydrodynamic diameter, it is expected that higher hydrodynamic diameter will lead to more open flocs (lower SE values), since the polymer chains are longer, allowing more free space between bridged particles. This hypothesis appears to only hold surely in the case of co-polymers. For ter-polymers no general trend can be observed. This suggests that hydrophobic interactions between the oil in the effluent and the polymer chain affect the flocs structure, and the shorter the flocculant molecule the more evident is this effect.

Similar trend of zeta potential and hydrodynamic diameter effects on SE (Figure 8) was verified when looking at charge density and molecular weight effects, respectively, as was previously shown for the influences on floc size (Figure 7). Thus, only plots for the influence of zeta potential and hydrodynamic diameter on SE are presented here.

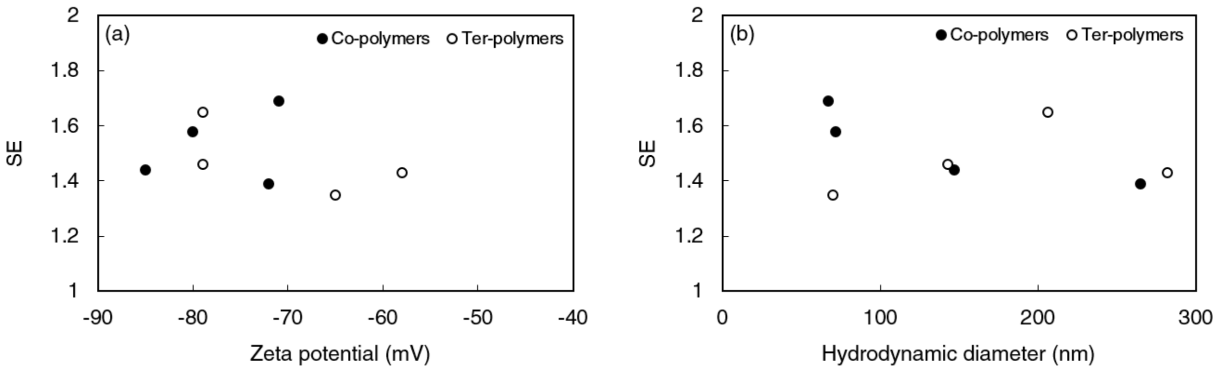

Figure 8 SE after 6 min as function of zeta potential (a) and hydrodynamic diameter (b) for the highest polyelectrolyte concentration tested (13 mg/L).

In Figure 9, floc size is plotted as a function of hydrophobic content of the polymer flocculant (for polyelectrolytes synthesized using the same organic phase (Carnation)), which is indicated by the molar ratio of monomer 3 in the polyelectrolyte composition. Each polymer series contains a different ratio of charged monomer within the polymer composition (0%, 1% and 3% as indicated in Table 1). For each polymer series, there is an increase of the maximum floc size with the addition of a small amount of hydrophobic content (1 mol%) to the initially fully hydrophilic composition, which then stabilizes or decreases when the hydrophobic content is increased to higher concentrations (3 mol%). This suggests that the presence of hydrophobicity is favorable for the flocculation process, though there is an optimum content that improves the floc size and above that value the presence of higher degree of hydrophobicity can be detrimental, in spite of the higher molecular weights obtained. This can be attributed, for instance, to a more difficult dissolution of the polymer. The improvement of flocculation performance in the presence of hydrophobically modified polyelectrolytes was already discussed in the literature for other formulations[22,30]. The affinity between the hydrophobic part of the polymer and the oil droplets in the effluent appears to significantly enhance the treatment efficiency, as observed in the present study.

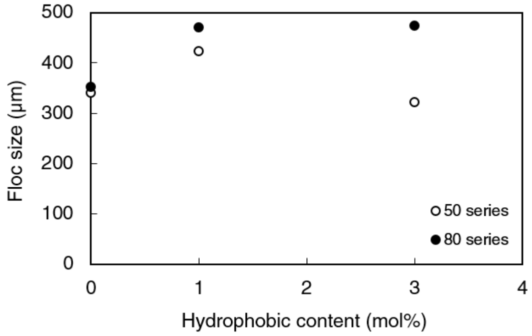

Figure 9 Floc size after 6 min, for the higher concentration tested (13 mg/L), as function of hydrophobic content quantified by the ratio (mol%) of monomer 3 in the polyelectrolyte composition.

CONCLUSIONS

The results obtained in this study suggest the viability of using the LDS technique to access and understand the flocculation progression in a real industrial oily effluent, and to determine some important floc characteristics under mild turbulent environment.

Anionic polyelectrolytes, varying in charge density, molar mass and hydrophobicity were tested in terms of performance in flocculation, encouraging the execution of further pilot scale testing under industrial conditions in order to confirm the suitability for the final application. The experimental technique used, which was tested for the first time in a real industrial effluent, allowed extracting information on the influence of the polyelectrolytes characteristics on the flocculation process. This can be extremely important in the future, when dealing with the selection/optimization of the right flocculant to treat a specific effluent, as well as the tuning of the operational conditions. As expected, results show that high molecular weight polyelectrolytes with medium to high charge density induce flocculation by bridging mechanism. Results also demonstrate the influence of increasing flocculant concentration: floc size increases and more porous aggregates are obtained. Polyelectrolytes characteristics proved to be critical in the floc size obtained. Higher zeta potential, hydrodynamic diameter and molecular weight lead to larger flocs. The effect of the hydrophobic content suggests that the presence of hydrophobicity is favorable for the flocculation process, however there is an optimum hydrophobic content that improves the floc size and above that value the effect is no longer beneficial.

AUTHOR INFORMATION

Corresponding Author

Maria G. Rasteiro (E-mail: mgr@eq.uc.pt)

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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REFERENCES

(1) Sonune, A.; Ghate, R. Developments in Wastewater Treatment Methods. *Desalination* **2004**, *167*, 55.

(2) Iselau, F.; Phan Xuan, T.; Trefalt, G.; Matic, A.; Holmberg, K.; Bordes, R. Formation and Relaxation Kinetics of Starch–particle Complexes. *Soft Matter* **2016**, *12*, 9509.

(3) Lee, C. S.; Robinson, J.; Chong, M. F. A Review on Application of Flocculants in Wastewater Treatment. *Process Saf. Environ. Prot.* **2014**, *92*, 489.

(4) Pavlovic, M.; Adok-Sipiczki, M.; Nardin, C.; Pearson, S.; Bourgeat-Lami, E.; Prevot, V.; Szilagyi, I. Effect of MacroRAFT Copolymer Adsorption on the Colloidal Stability of Layered Double Hydroxide Nanoparticles. *Langmuir* **2015**, *31*, 12609.

(5) Hierrezuelo, J.; Szilagyi, I.; Vaccaro, A.; Borkovec, M. Probing Nanometer-Thick Polyelectrolyte Layers Adsorbed on Oppositely Charged Particles by Dynamic Light Scattering. *Macromolecules* **2010**, *43*, 9108.

(6) Kleimann, J.; Gehin-Delval, C.; Auweter, H.; Borkovec, M. Super-Stoichiometric Charge Neutralization in Particle-Polyelectrolyte Systems. *Langmuir* **2005**, *21*, 3688.

(7) Ahmad, A.; Wong, S.; Teng, T.; Zuhairi, A. Improvement of Alum and PACl Coagulation by Polyacrylamides (PAMs) for the Treatment of Pulp and Paper Mill Wastewater. *Chem. Eng. J.* **2008**, *137*, 510.

(8) Caskey, J. A.; Primus, R. J. The Effect of Anionic Polyacrylamide Molecular Conformation and Configuration on Flocculation Effectiveness. *Environ. Prog.* **1986**, *5*, 98.

(9) Blanco, A.; Fuente, E.; Negro, C.; Tijero, J. Flocculation Monitoring: Focused Beam Reflectance Measurement as a Measurement Tool. *Can. J. Chem. Eng.* **2008**, *80*, 1.

(10) Eriksson, L.; Alm, B.; Stenius, P. Formation and Structure of Polystyrene Latex Aggregates Obtained by Flocculation with Cationic Polyelectrolytes. *Colloids Surfaces A Physicochem. Eng. Asp.* **1993**, *70*, 47.

(11) Biggs, S.; Habgood, M.; Jameson, G. J.; Yan, Y. Aggregate Structures Formed via a Bridging Flocculation Mechanism. *Chem. Eng. J.* **2000**, *80*, 13.

(12) Thomas, D. N.; Judd, S. J.; Fawcett, N. Flocculation Modelling: A Review. *Water Res.* **1999**, *33*, 1579.

(13) Dao, V. H.; Cameron, N. R.; Saito, K. Synthesis, Properties and Performance of Organic Polymers Employed in Flocculation Applications. *Polym. Chem.* **2016**, *7*, 11.

(14) Pinheiro, I.; Ferreira, P. J.; Garcia, F. A.; Reis, M. S.; Pereira, A. C.; Wandrey, C.; Ahmadloo, H.; Amaral, J. L.; Hunkeler, D.; Rasteiro, M. G. An Experimental Design Methodology to Evaluate the Importance of Different Parameters on Flocculation by Polyelectrolytes. *Powder Technol.* **2013**, *238*, 2.

(15) Rasteiro, M. G.; Garcia, F. A. P.; Ferreira, P.; Blanco, A.; Negro, C.; Antunes, E. The Use of LDS as a Tool to Evaluate Flocculation Mechanisms. *Chem. Eng. Process. Process Intensif.* **2008**, *47*, 1323.

(16) Rasteiro, M. G.; Garcia, F. A. P.; del Mar Pérez, M. Applying LDS to Monitor Flocculation in Papermaking. *Part. Sci. Technol.* **2007**, *25*, 303.

(17) Rasteiro, M. G.; Pinheiro, I.; Ferreira, P. J.; Garcia, F. A.; Wandrey, C.; Ahmadloo, H.; Hunkeler, D. Correlating Aggregates Structure with PEL Characteristics Using an Experimental Design Methodology. *Procedia Eng.* **2015**, *102*, 1697.

(18) Chakraborti, R. K.; Gardner, K. H.; Atkinson, J. F.; Van Benschoten, J. E. Changes in Fractal Dimension during Aggregation. *Water Res.* **2003**, *37*, 873.

(19) Liao, J. Y. H.; Selomulya, C.; Bushell, G.; Bickert, G.; Amal, R. On Different Approaches to Estimate the Mass Fractal Dimension of Coal Aggregates. *Part. Part. Syst. Charact.* **2005**, *22*, 299.

(20) Antunes, E.; Garcia, F. A. P.; Blanco, A.; Negro, C.; Rasteiro, M. G. Evaluation of the Flocculation and Reflocculation Performance of a System with Calcium Carbonate, Cationic Acrylamide Co-Polymers, and Bentonite Microparticles. *Ind. Eng. Chem. Res.* **2015**, *54*, 198.

(21) Liang, L.; Peng, Y.; Tan, J.; Xie, G. A Review of the Modern Characterization Techniques for Flocs in Mineral Processing. *Miner. Eng.* **2015**, *84*, 130.

(22) Bratskaya, S.; Avramenko, V.; Schwarz, S.; Philippova, I. Enhanced Flocculation of Oil-in-Water Emulsions by Hydrophobically Modified Chitosan Derivatives. *Colloids Surfaces A Physicochem. Eng. Asp.* **2006**, *275*, 168.

(23) Candau, F.; Selb, J. Hydrophobically-Modified Polyacrylamides Prepared by Micellar Polymerization. *Adv. Colloid Interface Sci.* **1999**, *79*, 149.

(24) Ren, H.; Chen, W.; Zheng, Y.; Luan, Z. Effect of Hydrophobic Group on Flocculation Properties and Dewatering Efficiency of Cationic Acrylamide Copolymers. *React. Funct. Polym.* **2007**, *67*, 601.

(25) Palomino, D.; Hunkeler, D.; Stoll, S. Comparison of Two Cationic Polymeric Flocculant Architectures on the Destabilization of Negatively Charged Latex Suspensions. *Polymer (Guildf).* **2011**, *52*, 1019.

(26) Lourenço, A.; Arnold, J.; Gamelas, J. A. F.; Rasteiro, M. G. A More Eco-Friendly Synthesis of Flocculants to Treat Wastewaters Using Health-Friendly Solvents. *Colloids Polym. Sci.* **2017**, *295*, 2123.

(27) Malvern Instruments, "Zetasizer Nano Series User Manual."

(28) Lee, K. E.; Morad, N.; Poh, B. T.; Teng, T. T. Comparative Study on the Effectiveness of Hydrophobically Modified Cationic Polyacrylamide Groups in the Flocculation of Kaolin. *Desalination* **2011**, *270*, 206.

(29) Rasteiro, M. G.; Garcia, F. A. P.; Ferreira, P. J.; Antunes, E.; Hunkeler, D.; Wandrey, C. Flocculation by Cationic Polyelectrolytes: Relating Efficiency with Polyelectrolyte Characteristics. *J. Appl. Polym. Sci.* **2010**, *116*, 3603.

(30) Lü, T.; Qi, D.; Zhao, H.; Cheng, Y. Synthesis of Hydrophobically Modified Flocculant by Aqueous Dispersion Polymerization and Its Application in Oily Wastewater Treatment. *Polym. Eng. Sci.* **2015**, *55*, 1.