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Anionic polyelectrolytes synthesized in aromatic free oils process for application as flocculants in dairy industry effluent treatment

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ABSTRACT

The wastewater generated from many industries contains suspended and dissolved solids, including organic and inorganic particles, metals and other impurities. Direct flocculation is regularly used to neutralize the charge of the colloidal particles and bridge the destabilized particles together to form flocs, in a cost and time-effective way.

This work refers to the development of new anionic flocculants (co and ter-polymers) tailored to be used in dairy effluents treatment, using a synthesis process in which new oil phases free of aromatics are applied. Regarding the ter-polymers, anionic polyacrylamides were synthesized in the presence of three different hydrophobic monomers, at different concentrations.

Flocculation performance was evaluated using an effluent from dairy industry. Results show that the developed polyelectrolytes are very promising additives for the treatment of the mentioned effluent. For optimized conditions, 95% turbidity reduction, 44% COD removal and 57% total solids removal were achieved, with only 53 mg/L of flocculant.

KEYWORDS

Polyelectrolytes, wastewater treatment, flocculation, oily wastewater, dairy industry effluent.

INTRODUCTION

Flocculation is a simple and economic treatment strategy that, in suitable conditions can be applied to the treatment of several different effluents. In this process, firstly a flocculant is added, which will drive the aggregation or agglomeration of finely divided or dispersed particles, thus forming larger particles. Secondly, these particles aggregates, rapidly settle and the system becomes clarified[1]. Wastewater treatment using this method is efficient and is widely used for wastewater from various sources, such as textile industry, palm oil mill, pulp mill, and others[2–5].

Synthetic polymers have been commonly used as flocculants to enhance the flocculation process efficiency[6]. Linear, water soluble polyelectrolytes, based on repeating units of monomers like acrylamide and acrylic acid, are typical commercial organic flocculants. Important polymer flocculant characteristics such as molecular weight, structure (linear or branched), charge density, charge type and composition can vary widely, but generally the polymers can be divided into four main categories based on their charge:cationic (positively charged), anionic (negatively charged), amphoteric (positively and negatively charged) and non-ionic (without charge), where these ionic polymers are commonly named polyelectrolytes. Flocculation efficiency is significantly affected by the nature of the charges, molecular weight and charge density of the polyelectrolyte[7].

The efficiency of aggregation using organic polyelectrolytes can be much higher than with inorganic coagulants. Even in low dosages, polyelectrolytes can effectively promote floc growth and improve separation efficiency[8]. Cationic polyelectrolytes have been more often reported in literature as flocculant agents because of the tendency of solid surfaces to acquire a negative charge[9]. Yet, a non-negligible proportion of solid impurities in wastewaters are positively charged, but their flocculation with anionic polyelectrolytes have received less attention, and consequently a much narrower variety of anionic polyelectrolyte flocculants is available.

Anionic polyelectrolytes can be used in the treatment of municipal wastewaters and effluents from industries of mineral processing, tanning, sugar processing, paper production, metal working and gravel washing[10]. Most of the commercial anionic flocculants present carboxylate and sulfonate ions in their structure as functional groups and are often copolymers of acrylamide (AAm).

Synthetic polyelectrolytes such as polyacrylamide and its copolymers have attracted much attention as flocculants for wastewater treatment. Polyelectrolytes with high molecular weight and medium to high charge densities have been applied as flocculants in direct flocculation or combined with inorganic coagulants like alum, ferric chloride or ferric sulphate. The addition of inorganic compounds stimulates the destabilization of colloidal materials and promotes the agglomeration of small particles into larger flocs able to settle[1].

The synthesis processes of the above-mentioned anionic polymeric flocculants usually employs aliphatic mineral oils as continuous phase. Examples of hydrocarbon fluids applied for many years in this type of synthesis include mixtures of normal paraffins, iso-paraffins, cyclo-paraffins and aromatics[11–13]. However, the presence of aromatic components, even at levels as low as 0.01 wt%, does not meet health or environmental regulations, exhibiting human and aquatic toxicity levels[12]. Still, the organic phase used in inverse-emulsion polymerization must have low content in highly unsaturated components and high density, to avoid sedimentation of the emulsion. Alternative continuous phases may include white mineral oils or hydrogenated polyalphaolefins. Health-friendly formulations for production of polyelectrolytes by inverse-emulsion polymerization were reported in a previous work[14]. The synthesis process comprises alternative oils, the main characteristics being non-irritating, high boiling point, high stability and high purity, free of harmful ingredients, like aromatic and metal compounds. These oils draw large interest from industry due to their physical properties and level of purity, which is often a restriction for use in personal care, food and pharmaceutical products[15]. Also, new cationic polyelectrolytes have been previously synthesized by the authors using the new health-friendly formulations, as reported in Lourenço et al.[16], which were then tested in the treatment of an olive oil mill effluent.

Nowadays, the dairy industry is considered as one of the most polluting food industries, due to the high demand for milk and derived products, the large water consumption in cleaning and washing operations and the characteristics of the resulting effluent[17]. Presence of fats, nutrients, lactose, detergents and sanitizing agents can cause serious environmental problems, affecting the aquatic life and leading to eutrophication of receiving waters[17]. In addition, since the dairy industry produces several different products, such as milk, cheese, butter, yogurt or ice-cream, the raw effluent can vary broadly in quantity and composition[18,19]. Furthermore, wide ranges of pH, concentration of solids, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) have been reported in the literature[20]. These aspects show how complex is the treatment of this type of wastewater and the necessity for studies using innovative treatment techniques, considering their environmental sustainability.

Biological methods are typically applied to treat dairy effluents, suitable for the presence of high organic matter, often combined with physico-chemical treatment processes, required to remove suspended, colloidal, and dissolved constituents. Activated sludge process, aerated lagoons, trickling filters, sequencing batch reactor, anaerobic sludge blanket reactor or anaerobic filters, in combination with coagulation/flocculation with various inorganic additives or organic polymers are some examples[21].

Anaerobic treatment seems to be the most widely used process for the treatment of dairy wastewaters. Nevertheless, not all compounds of a dairy effluent are biodegradable; for example protein and long-chain fatty acids are not easily degraded as a result of their inhibitory effect to methanogenic bacteria[22,23]. Thus, additional treatment is typically required. Aerobic treatment methods are high energy-demanding processes, resulting in physico-chemical treatment processes being frequently applied as primary clarification procedure of dairy effluents treatment instead.

Coagulation and flocculation processes are of greatest importance and widely used due to their simplicity and effectiveness[24]. Addition of coagulants and flocculants can also improve filtration performance, by reducing the organic matter and the amount of suspended and colloidal particles, responsible for the turbidity of the effluent[25,26]. This treatment method can be applied in previously anaerobically treated dairy wastewater or in raw dairy effluent[27]. The ability of conventional salts and polymeric inorganic coagulants for the treatment of different kinds of dairy wastewater has also been studied[28,29].

Rusten et al.[30] tested four different combinations of coagulants/flocculants in the treatment of dairy wastewaters. Using $FeClSO_4$ showed the best results, removing 2–3% more COD than H_2SO_4 combined with carboxymethyl cellulose, and 4–6% more COD than lactic acid combined with carboxymethyl cellulose. Selmer-Olsen et al.[31] applied different types of chitosan as treatment product for the same purpose and achieved nearly 60% removal of COD and 90% removal of particles, for dosages of 5-15 mg/L at pH 4.5-5. Sarkar et al.[32] applied chitosan followed by adsorption with powdered activated carbon in treating dairy wastewater before membrane separation method. At pH 4.0, the reductions were 48% in total dissolved solids and 57% in COD with a 10-50 mg/L chitosan dosage. Kushwaha et al.[29] reported the treatment of a simulated dairy wastewater by inorganic coagulants such as polyaluminum chloride, ferrous sulphate ($FeSO_4$) and potassium alum ($KAl(SO_4)_2 \cdot 12H_2O$). Optimum pH was found to be 8.0, and 300, 800 and 500 mg/L of polyaluminum chloride, $FeSO_4$ and $KAl(SO_4)_2 \cdot 12H_2O$, respectively, resulted in 69.2, 66.5 and 63.8% of COD removal efficiency. Tchamango et al.[33] compared electrocoagulation with chemical coagulation with aluminum sulphate. Both gave similar removal rates for nitrogen and turbidity; however, the removals of phosphorus and COD were slightly higher by chemical coagulation. The turbidity was practically eliminated, while phosphorus, nitrogen, and COD were reduced up to 94, 81 and 63% respectively, at concentrations of coagulant above 950 mg/L. Rivas et al. [28] treated cheese wastewater by means of a coagulation−flocculation process with three different coagulants, ferrous sulfate ($FeSO_4$), aluminum sulfate ($Al_2(SO_4)_3$), and ferric chloride ($FeCl_3$). The optimum conditions for $FeSO_4$ were obtained using 250 mg/L at pH 8.5 and 50% of COD was removed. $Al_2(SO_4)_3$ achieved slightly lower reductions of COD, however the amount needed was significantly higher (1000 mg/L). With $FeCl_3$, similar results to those obtained with $FeSO_4$ were verified: 250 mg/L was enough to eliminate COD in the range of 40−60%, depending on the operating conditions. Formentini-Schmitt et al.[27] investigated the pretreatment of dairy industry wastewater by coagulation/flocculation/sedimentation using Moringa oleifera as coagulant. The efficiency of the pretreatment step with a coagulant concentration of 1500 mg/L was of 97.6% for turbidity reduction and 39.4% for COD removal. Prakash et al.[34] studied the effectiveness of coagulation and Fenton's oxidation in a simulated dairy wastewater. Individually, coagulation resulted in 67% COD removal, with a ferrous sulphate dosage of 800 mg/L at pH 6.0. Loloei et al.[35] studied the effect of different types of coagulants such as inorganic alum and ferrous sulphate and polymeric flocculants (anionic polyacrylamide (PAA) and polyferric sulphate (PFS)) on the treatment of a simulated dairy wastewater. The optimum conditions for alum and ferrous sulphate were 1000 mg/L and pH 5.0, and in these conditions, COD removal efficiency was 68 and 62%, respectively. Turbidity removal was 95% turbidity in both cases. When Alum was used combined with PFS or PAA as coagulants aid (20 mg/l), 82% decrease in COD was obtained using a low dose of Alum (100 mg/L). In another study Girish et al.[36] analysed the performance of a polyamine salt used as cationic coagulant, and a polyacrylamide salt of medium and high molecular weight used as anionic and nonionic polyelectrolytes, in a real dairy industry wastewater treatment. With increase in pH, the optimum polyelectrolyte dose was found to decrease. The three salts led to similar performances (45-48% turbidity reduction), even if the higher molecular weight polyacrylamide required a lower dosage to be effective.

Aysegul Tanik et al.[37] investigated $FeCl_3$, $FeSO_4$ and alum as coagulants for the treatment of dairy wastewater originating from a dairy products plant. Optimum coagulant dosage was determined as 200 mg/L for all the coagulants tested with optimum pH values of 4-4.5 for $FeCl_3$ and $FeSO_4$, and 5- 6 for alum. Maximum overall COD removal efficiencies were obtained as 72, 59 and 54% for $FeCl_3$, $FeSO_4$ and alum, respectively. Most of the flocculation processes in dairy effluents use inorganic or natural-based products, requiring higher amounts of additives and, in general, providing only moderate reduction of the important parameters (COD and turbidity). Thus, there is still a need for flocculants with distinct characteristics, immediately soluble in aqueous systems, highly efficient in little quantities and that generate large and strong flocs, leading to a good settling performance.

Metal salts are effective coagulants by hydrolysis of monomeric and polymeric species that will neutralize the surface of the colloids and soluble particles and thus destabilize them. However, wastewater from the dairy industry treated with conventional coagulation requires large amounts of reactive inorganic chemicals and generates large volumes of nonbiodegradable sludge[20]. Moreover, coagulants from natural sources may not be appropriate for the treatment of industrial dairy wastewaters due to their low availability in large-scale, and the challenges associated with using them in different environments and the varied range of wastewater characteristics. Furthermore, polymer flocculants, especially ionic polymers, can destabilize colloids through surface neutralization, particle bridging and floc growing, improving the efficiency of settling and filtration. However, only few studies are reported in the open literature for their application in the flocculation of dairy wastewater.

To achieve the highest flocculant's performance with low doses, specific designed products for a target wastewater should be developed. In the present study, we synthesized anionic polymer flocculants via health-friendly processes and explore their ability to treat a dairy effluent in a flocculation process. Twelve distinct hydrophobically modified terpolymer compositions were prepared with different hydrophobic chain length and different hydrophobic component content. Their performance as flocculants of dairy wastewaters was then evaluated via turbidity reduction, COD and total solids removals and compared with that of the corresponding copolymers containing no hydrophobic monomer. The decision in the present work was to focus on a dairy effluent, considering the considerable magnitude of the dairy industry in Portugal and in other European countries, motivated by consumers' needs. In the future applications in other oily effluents will also be studied.

EXPERIMENTAL SECTION

Materials

Acrylamide (AAm) solution, at 50 wt%, was purchased from Kemira (Botlek, Netherlands). The acrylamido-2-methyl-1-propanesulfonic acid sodium salt (Na-AMPS) solution, at 50 wt%, was purchased from Lubrizol (Bradford, UK) and used as received. Stearyl methacrylate (SMA) was purchased from BASF (Ludwigshafen, Germany). Ethyl acrylate (EA) and lauryl methacrylate (LMA) were purchased from Evonik (Darmstadt, Germany). Tert-butyl hydroperoxide (TBHP) was purchased from Acros Organics (Geel, Belgium). Sodium metabisulfite (MBS) was purchased from Brenntag (Esseco, Italy). Diethylenetriaminepentaacetic acid pentasodium salt solution (Pentasodium DTPA) was purchased from Keininghaus Chemie (Essen, Germany). 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). Sodium chloride (NaCl), n-hexane, acetone and isopropanol were purchased from VWR (Leuven, Belgium). The oily wastewater tested was an effluent obtained from a dairy industry (Lactogal Produtos Alimentares S.A., Portugal), and its characteristics are summarized in Table 1.

Table 1 Characteristics of the dairy effluent sample tested before any treatment.

Parameter	Value
pH	11.7
COD (gO_2/L)	3.3
Total solids (g/L)	6.2
Turbidity (NTU)	680

Inverse-emulsion polymerization

The procedure for the inversion-emulsion polymerization follows what has been described in the previous papers. Before starting the reaction, the aqueous phase was prepared using deionized water, acrylamide, Na-AMPS and 0.625 wt% of adipic acid for hydrolytic stability of the polymers. The total monomer level of the initial emulsion was 34.0 wt% and the copper in the reagents was chelated by adding 334 ppm of Pentasodium DTPA[16]. Carnation and Puresyn4 were used as organic phases[14,16]. Sorbitan isostearate and PEG-7 Hydrogenated castor oil were used as surfactants and blended in the suitable ratio in order to obtain a hydrophilic–lipophilic balance (HLB) between 4.75 and 5.75, depending on the monomers percentage and oil phase used. The inverse-emulsion polymerization[14,16,38] of the polyelectrolytes was performed in a 500 mL glass reactor and the aqueous phase was added to the organic phase under mechanical stirring for 30 min. For the synthesis comprising hydrophobic monomers, the suitable amount of hydrophobic monomer, EA, LMA or SMA, was added at this moment to the inverse-emulsion prepared. This emulsion was degassed with nitrogen for 60 min under mechanical stirring (700 rpm), at room temperature. The initiator redox chemicals used were TBHP and sodium MBS. The polymerization was initiated in all the cases by injecting an aqueous solution with 100 ppm of TBHP to the mixture and after a 1.0 wt% solution of sodium MBS. The peak temperatures achieved in the reactions were between 41 and 57 ºC. At the end of the polymerization, additional amounts of the initiatiors (TBHP and sodium MBS) were added in order to scavenge residual monomer. When the temperature of the mixture in the reactor decreased to 32 ºC, 2.20 wt% of wetting agent Synperonic LF/30 was added to help the inversion of the polyelectrolyte when added to water. Figure 1 presents a schematic representation of the final copolymer, Poly(AAm-Na-AMPS), and terpolymers, Poly(AAm-Na-AMPS-EA), Poly(AAm-Na-AMPS-LMA) and Poly(AAm-Na-AMPS-SMA).

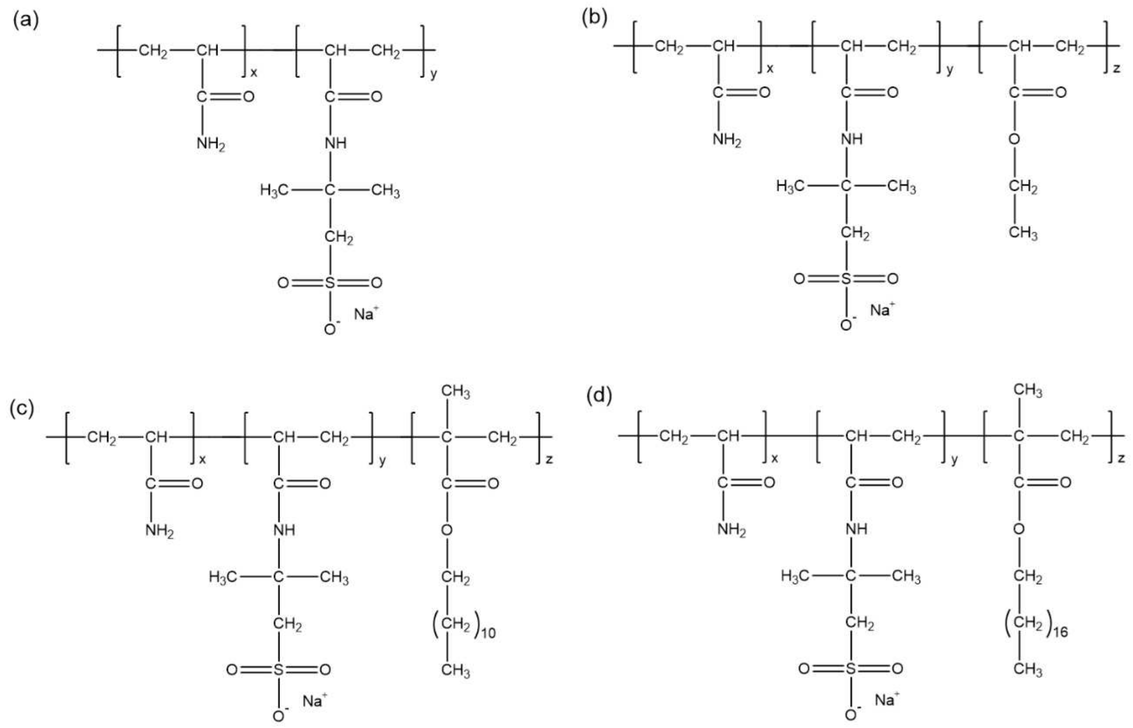

Figure 1 Schematic molecular structure of the final polymers obtained: Poly(AAm-Na-AMPS) (a), Poly(AAm-Na-AMPS-EA) (b), Poly(AAm-Na-AMPS-LMA) (c) and Poly(AAm-Na-AMPS-SMA) (d).

Isolation of polymers

Isolation of polymers for further characterization was performed by diluting 3 g of emulsion in 9 mL of hexane and following addition to a mixture of 240 mL of acetone and 18 mL of isopropanol under stirring. After 15 min, the mixture was filtered under vacuum and the precipitate washed with fresh acetone. The samples were dried in an oven at 60 ºC overnight and stored in a desiccator. Table 2 summarizes the initial composition of the synthesized polyelectrolytes. Lower anionic fraction is represented as the 50 series, while higher anionic fraction is represented as the 80 series. C and P series in the list refer to the use of Carnation and Puresyn4, respectively, as the aromatic free synthesis medium. In the case of terpolymers, 1 and 3 represent the respective amount of hydrophobic monomer introduced in the feed mixture, and only Carnation was used as organic phase.

Table 2 Summary of the polyelectrolytes initial composition based on the mass balance of the feed mixture. Poly(AAm-Na-AMPS): 50AC, 80AC, 50AP and 80AP. Poly(AAm-Na-AMPS-EA): 50A1EC, 50A3EC, 80A1EC and 80A3EC. Poly(AAm-Na-AMPS-LMA): 50A1LC, 50A3LC, 80A1LC and 80A3LC. Poly(AAm-Na-AMPS-SMA): 50A1SC, 50A3SC, 80A1SC and 80A3SC.

Polymer designation	AAm ratio		Na-AMPS ratio		Hydrophobic 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
50A1LC	48.5	74.0	48.5	25.0	3.0	1.0	Carnation
50A3LC	47.0	73.0	47.0	25.0	6.0	3.0	Carnation
80A1LC	19.0	41.0	79.0	58.0	2.0	1.0	Carnation
80A3LC	17.5	39.0	77.5	58.0	5.0	3.0	Carnation
50A1SC	48.0	74.0	48.0	25.0	4.0	1.0	Carnation
50A3SC	46.0	72.0	46.0	25.0	8.0	3.0	Carnation
80A1SC	19.0	41.0	79.0	58.0	2.0	1.0	Carnation
80A3SC	17.0	38.0	77.0	59.0	6.0	3.0	Carnation

Polyelectrolytes characterization

The charge density of the polyelectrolytes was determined by elemental analysis using an element analyser EA 1108 CHNS-O from Fisons and 2,5-bis(5-tert-butyl-benzoxazol-2-yl) thiophene as standard. The elements C, H, N and S were analyzed and the S element content was used for the calculation of the anionic fraction. At least three measurements for each sample were performed.

The FTIR spectra were acquired on a Bruker Tensor 27 spectrometer, equiped with an attenuated total reflection (ATR) MKII Golden Gate accessory with a diamond crystal 45º top plate. The spectra were recorded in the 500-4000 cm^{-1} range with a resolution of 4 cm^{-1} and a number of scans of 128. Polymers in the powder state were used for the measurements.

The ^{1}H NMR spectra were acquired on a Bruker Avance III 400 MHz NMR spectrometer. Deuterium oxide at about 5% (w/v) concentration was used to dissolve the samples at room temperature which were then placed inside 5 mm NMR tubes. ^{1}H NMR spectra were recorded at 25 ºC and sodium 3-(trimethylsilyl)propionate-d_4 was used for reference signals.

Dynamic light scattering (DLS), static light scattering (SLS) and electrophoretic light scattering were used to determine hydrodynamic diameter, molecular weight and zeta potential, respectively, of the isolated polymers, in a Malvern Zetasizer Nano ZS, ZEN3600 model (Malvern Instruments Ltd, UK). In the case of hydrodynamic diameter determination, stock solutions were prepared with concentrations of 0.05 g/L for copolymers and 0.03 g/L for terpolymers, using ultrapure water and allowed to stir overnight. The samples were filtered through 0.45-μm syringe filters before introduction into the analysis glass cell. The temperature was set to 25 ºC for the measurements and at least three measurements for each sample performed. Backscatter detection was used with an angle of 173º angle. Evaluation of molecular weight was performed for each polymer using stock solutions (0.5 g/L) prepared in NaCl 0.5 M and agitated overnight. Dilution of the stock solution was required to obtain the samples for analysis, with concentrations from 0.5-0.02 g/L. Again, all samples were filtered using 0.45-μm syringe filters. Toluene was the solvent used as standard. Refractive index was preciously determined for each concentration, using a refractometer Atago RX-5000D, and a plot of refractive index versus concentration was necessary to obtain dn/dc (variation of refractive index with concentration), as required by the SLS software. From the SLS measurements the Debye plot was produced according to the Rayleigh equation [39], which provided information about the weight-average molecular weight of the polymers. Zeta potential was determined by using 1 mL of stock solution (0.1 g/L) in ultrapure water for each polymer, which was carefully injected with a syringe into a folded capillary cell. At least three replicate measurements were performed for each sample.

Evaluation of flocculation efficiency in industrial effluents

200 ml of polymer solutions at 0.4 wt% concentration were prepared in distilled water, under magnetic stirring for sixty minutes. Samples with 75-mL of pre-agitated industrial effluent were adjusted to three different pHs using hydrochloric acid (HCl) or sodium hydroxide (NaOH) aqueous solutions. pH was measured with a pH meter SCAN3BW (Scansci). Samples with different volumes of polymer solution were added to the wastewater, increasing successively the flocculant concentration from 13 mg/L till a maximum value of 104 mg/L. After each addition, the mixture was manually mixed for 10 seconds and allowed to settle for 2 min. Turbidity of the supernatant water was evaluated (minimum three repetitions), with a Photometer MD600 (Lovibond, UK). The uncertainty in the measurements was below 1.0% for all the samples. The previous range of concentrations was selected according with pre-screening tests performed starting with a concentration below the one necessary to have any flocculation and finishing when there is no further turbidity reduction by increasing the flocculant concentration. The total solids content and chemical oxygen demand of the supernatant of treated waters were accessed for the polyelectrolytes that showed higher performance in turbidity. A sample of a commercial flocculant (AlpineFloc Z1, a high molecular weight anionic polyacrylamide with 50 wt% charged fraction) usually used for this type of treatment, was provided by Aqua+Tech Specialities SA (Geneva, Switzerland) and tested as a reference, in the same conditions as the polymers developed here.

RESULTS AND DISCUSSION

Polyelectrolytes characterization

Charge density of polyelectrolytes was assessed by elemental analysis, using the S content as reference for the quantification of the sulfonate-containing anionic units (Table 3). Results confirm the viability of using health-friendly formulations to produce the desired polyelectrolytes, as reported already for other situations[14,16]. Generally, all polyelectrolytes presented lower anionic fraction than the theoretical value estimated from the ratios of monomers at the start of the reaction. These discrepancies are typically justified by the different reactivity ratios of the monomers in the copolymerization and/or by a possible incomplete polymerization due to the presence of oxygen molecules in the synthesis, interfering with the radical polymerization. When comparing polyelectrolytes prepared with and without hydrophobic monomer, one can observe a slightly lower anionic fraction for the hydrophobically modified samples (terpolymers) than for the equivalent copolymers (e.g. compare 50AC with 50A1EC, 50A3EC, 50A1LC, 50A3LC, 50A1SC and 50A3SC in Table 3), indicative of a lower reactivity of the anionic monomer. Two different organic phases were tested for the synthesis of the Poly(AAm-Na-AMPS) copolymers, however since both formulations led to similar compositions, and Carnation oil is economically more accessible, the latter was chosen as a continuous phase for all the subsequent syntheses in this study.

Table 3 Anionic fraction s calculated from the initial mass balance and estimated by elemental analysis. Poly(AAm-Na-AMPS): 50AC, 80AC, 50AP and 80AP. Poly(AAm-Na-AMPS-EA): 50A1EC, 50A3EC, 80A1EC and 80A3EC. Poly(AAm-Na-AMPS-LMA): 50A1LC, 50A3LC, 80A1LC and 80A3LC. Poly(AAm-Na-AMPS-SMA): 50A1SC, 50A3SC, 80A1SC and 80A3SC.

Polymer designation	Anionic fraction from the initial mass balance (wt%)	Anionic fraction estimated from elemental analysis (wt%)
50AC	50	41.5 ± 0.2
80AC	80	62.9 ± 0.5
50AP	50	41.9 ± 2.3
80AP	80	68.1 ± 2.1
50A1EC	49.4	39.5 ± 0.4
50A3EC	48.5	39.7 ± 1.2
80A1EC	79.7	62.2 ± 1.7
80A3EC	79	61.6 ± 1.5
50A1LC	48.5	41 ± 0.2
50A3LC	47	39 ± 4.6
80A1LC	79	57 ± 3.3
80A3LC	77.5	63 ± 0.3
50A1SC	48	41 ± 2.1
50A3SC	46	41 ± 1.5
80A1SC	79	58 ± 0.6
80A3SC	77	57 ± 0.3

The developed polyelectrolytes were characterized by ATR-FTIR spectroscopy (Figure 2). The spectra of all the polymers showed bands at ca. 3330 cm^{-1} and 3200 cm^{-1}, attributed to the N-H stretching vibrations in the monomeric units. The characteristic amide I band (C=O stretching in the amide groups) of the acrylamide and Na-AMPS appeared at 1656-1660 cm^{-1}. A shoulder at ca. 1620 cm^{-1} due to the amide II band of acrylamide was also observed in the spectra of the polymers with a higher content of acrylamide (namely for 50 series). Bands showing the presence of Na-AMPS were observed at 1543 cm^{-1} (amide II), 1184 cm^{-1} (asymmetric stretching of $S(=O)_2$), 1042 cm^{-1} (symmetric stretching of $S(=O)_2$), and 625 cm^{-1} (S-O stretching), with an increased intensity for the samples with a higher content of Na-AMPS (80 series). FTIR spectra of 50AC and 50AP were similar to each other, as well as spectra of 80AC and 80AP, confirming that there is no influence of the oil used as synthesis medium in the copolymerization reactions.

The incorporation of a low content of a third monomer was revealed by FTIR in a few cases. For the samples containing ethyl acrylate, the spectra were close to those of the 50AC and 80AC samples, and the detection of the hydrophobic component was not possible. As for the samples prepared with the addition of lauryl methacrylate, in spite of the fact that this hydrophobic monomer possesses a structure with a larger number of methylene (-CH2-) groups in the aliphatic chain, it was also not possible to identify this monomer unambiguously by ATR-FTIR spectroscopy. Indeed, the spectra recorded for sample 50A1LC and 50A3LC were similar to that of 50AC and the spectra of 80A1LC and 80A3LC were similar to that of 80AC. In both cases, the hydrophobic units appear to be present at levels below the sensitivity of the FTIR equipment. Alternatively, the bands corresponding to the hydrophobic monomers are masked by those from the major constituents of the polymers. On the other hand, the spectra of the samples 50A3SC and 80A3SC (Figure 2) prepared with 3 mol% of stearyl methacrylate in the synthesis were distinguishable from the spectra of 50AC and 80AC, respectively. In particular, changes were noted in the region of 2800-3000 cm-1, by the appearance of two new bands at 2923 and 2853 cm-1, which can be assigned to the asymmetric and symmetric stretching of the CH2 groups of the incorporated hydrophobic chain. A shoulder was also observed at ca. 1730 cm-1, due to the C=O stretching in the ester bonds of the hydrophobic unit. For the samples 50A1SC and 80A1SC prepared with 1 mol% of added stearyl methacrylate these differences were less distinguishable and the spectra were closer to those of the copolymers without added stearyl methacrylate (50AC and 80AC).

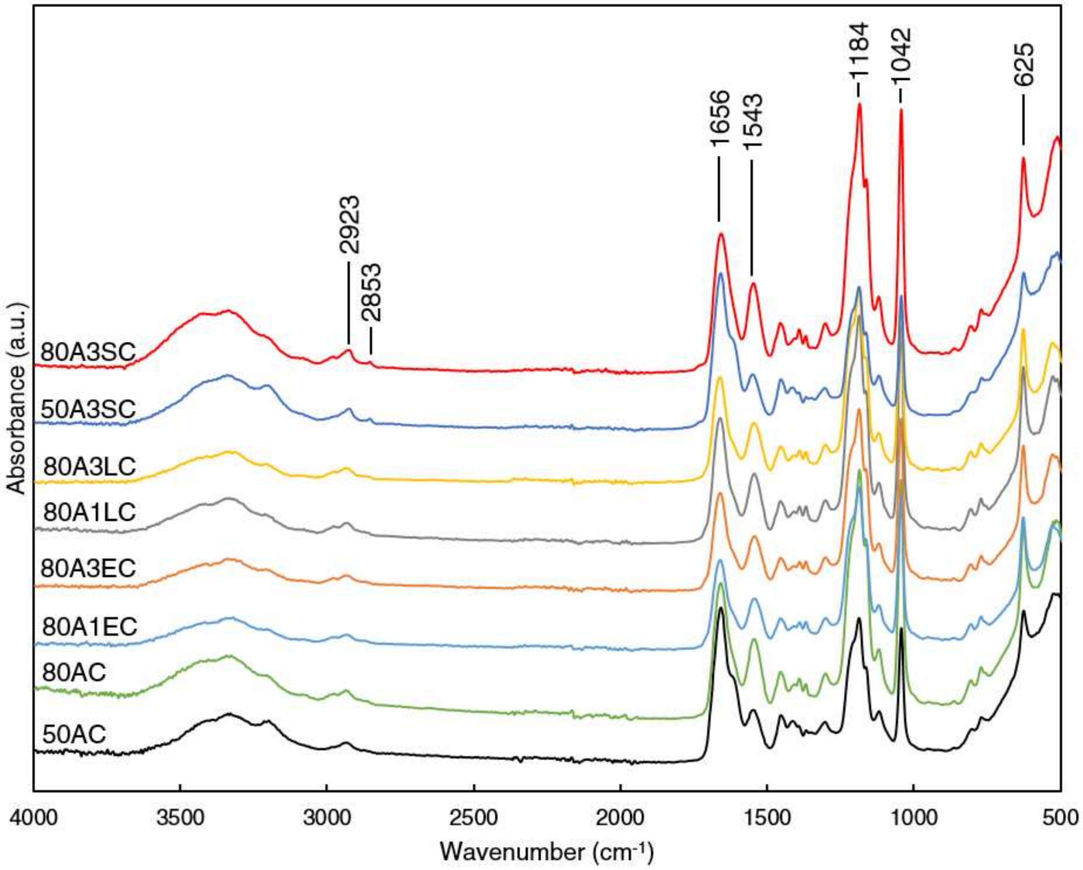

Figure 2 ATR-FTIR spectra examples for some of the polyelectrolytes prepared. Poly(AAm-Na-AMPS): 50AC and 80AC. Poly(AAm-Na-AMPS-EA): 80A1EC and 80A3EC. Poly(AAm-Na-AMPS-LMA): 80A1LC and 80A3LC. Poly(AAm-Na-AMPS-SMA): 50A3SC and 80A3SC.

^{1}H NMR spectroscopy was used to obtain additional insight on the presence of the hydrophobic components in the polymers. First we consider samples from the 80AC series with addition of the EA and LMA monomers. The spectrum of sample 80AC showed signals at 3.33, 2.15, 2.03 and 1.43 ppm (Figure 3), which can be assigned to methylene (-CH_2-) protons next to the sulfonic acid groups of the Na-AMPS, CH and CH_2 protons in the linear chain of the copolymer and methyl (CH_3) protons from the Na-AMPS. For samples 80A1EC, 80A3EC, 80A1LC and 80A3LC, where monomers EA and LMA were added to the synthesis mixture, new signals arose in the 1H NMR spectra, including a small intensity signal at 3.94 ppm and a signal at 1.10 ppm. The intensities of these new peaks increased with hydrophobic monomer content in both terpolymer series (Figure 3). These two signals can be attributed to the methylene protons in the O-CH2-C linkages (at 3.94ppm) and to the CH3 protons of the EA chain or to the (CH2)10 protons of the LMA chain (at 1.10ppm). The intensity of the signal at 2.15 ppm also increased greatly for these four samples in comparison to 80AC. Thus, although not observable by FTIR spectroscopy, the presence of EA and LMA units in the terpolymers could be confirmed by 1H NMR.

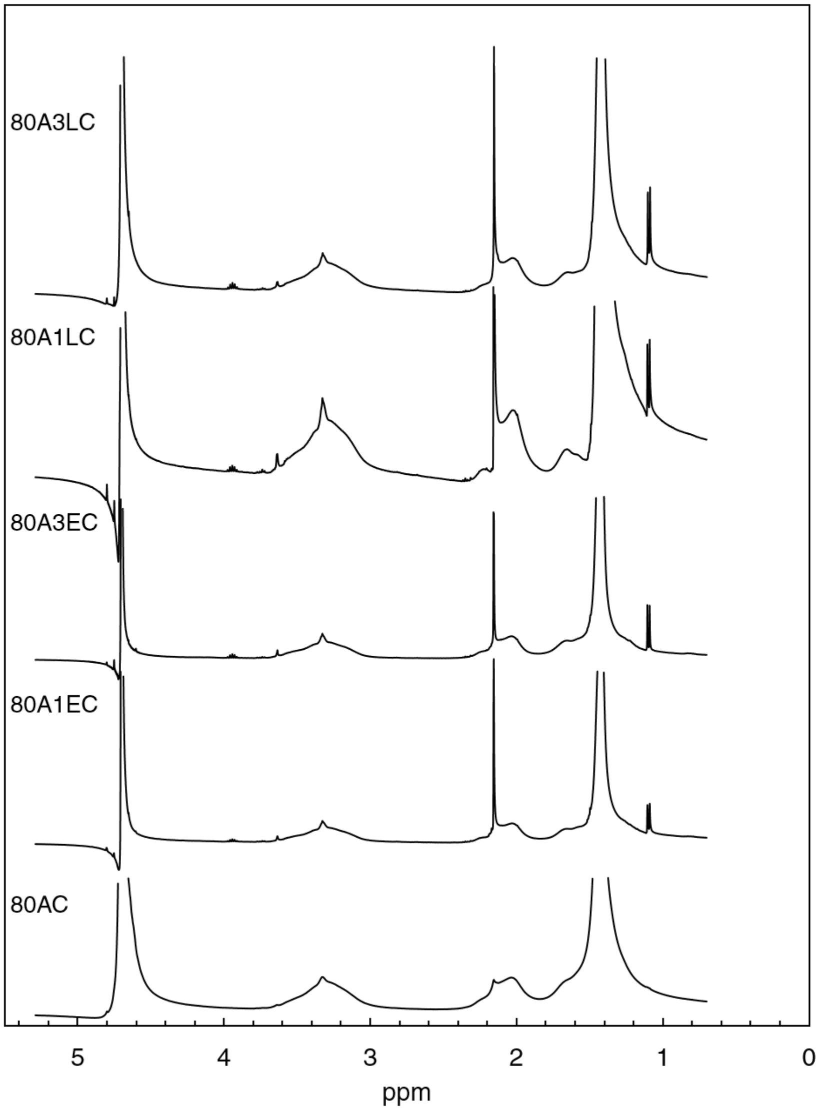

Figure 3 ^{1}H-NMR spectra for some of the polyelectrolytes prepared. Poly(AAm-Na-AMPS): 80AC. Poly(AAm-Na-AMPS-EA): 80A1EC and 80A3EC. Poly(AAm-Na-AMPS-LMA): 80A1LC and 80A3LC.

Results obtained for zeta potential, hydrodynamic diameter and molecular weight measurments for all polyelectrolytes are presented in Table 4. Zeta potential values are in reasonable accordance with charge density results (Table 3) determined by elemental analysis. Polymers of the 50 series have lower charge density and lower zeta potential (in absolute value) than polymers of the 80 series. Within the same series, it is possible to observe a decrease in zeta potential for the hydrophobically-modified polymers, with the exception of the three samples synthesized in the presence of the hydrophobic monomer stearyl methacrylate (50A3SC, 80A1SC and 80A3SC). In the remaining terpolymers, the decrease of zeta potential when compared to the corresponding copolymers can be due to the steric hindrance promoted by the aliphatic chain of the hydrophobic monomer, which can affect the anionic monomer addition to the chain.

Table 4 Polyelectrolytes characterization: zeta potential, hydrodynamic diameter and molecular weight. Poly(AAm-Na-AMPS): 50AC, 80AC, 50AP and 80AP. Poly(AAm-Na-AMPS-EA): 50A1EC, 50A3EC, 80A1EC and 80A3EC. Poly(AAm-Na-AMPS-LMA): 50A1LC, 50A3LC, 80A1LC and 80A3LC. Poly(AAm-Na-AMPS-SMA): 50A1SC, 50A3SC, 80A1SC and 80A3SC.

Polymer designation	Zeta Potential (mV)	Hydrodynamic diameter (nm)	Molecular weight (10^6 Da)
50AC	-71 ± 2	67 ± 2	0.9 ± 0.07
80AC	-80 ± 1	72 ± 1	1.0 ± 0.08
50AP	-72 ± 1	265 ± 37	2.5 ± 0.09
80AP	-85 ± 1	147 ± 4	1.3 ± 0.2
50A1EC	-65 ± 2	70 ± 1	0.6 ± 0.02
50A3EC	-58 ± 1	282 ±32	3.5 ± 0.07
80A1EC	-79 ± 1	143 ± 10	1.5 ± 0.2
80A3EC	-79 ± 2	206 ± 22	2.4 ± 0.08
50A1LC	-66 ± 1	129 ± 10	1.4 ± 0.007
50A3LC	-64 ± 1	209 ± 28	2.5 ± 0.3
80A1LC	-75 ± 1	174 ± 28	2.2 ± 0.2
80A3LC	-78 ± 1	124 ± 13	0.8 ± 0.03
50A1SC	-69 ± 1	219 ± 19	2.4 ± 0.1
50A3SC	-72 ± 1	180 ± 14	1.3 ± 0.1
80A1SC	-84 ± 1	132 ± 7	1.1 ± 0.007
80A3SC	-84 ± 1	81 ± 18	0.7 ± 0.2

For the same molecular weight and hydrophobicity, hydrodynamic diameter in water should increase consistently with zeta potential, since the repulsion between the molecule sites increases. However, for these specific polymers, the molecular weight range was wide, since the size of the polymer is influenced by many factors in the polymerization process, preventing a direct correlation between hydrodynamic diameter and zeta potential results. In a singular case of polymers 50AC, 80AC and 80AP, which have similar molecular weight, the tendency is verified and the hydrodynamic diameter increases with the increase of zeta potential. Furthermore, as expected, there is a correlation between hydrodynamic diameter and molecular weight, for polyelectrolytes with similar charge density, for which both values increase in parallel.

The introduction of hydrophobic molecules in the chain seems to have also some influence in the molecular weight of the polymer, especially at higher hydrophobic content. For polyelectrolytes prepared with 3 mol% of hydrophobic monomer, using hydrophobic monomers with higher number of methylene groups in the aliphatic chain (LMA and SMA), a decrease of the final molecular weight is observed (compare 50A3EC, 50A3LC and 50A3SC, and 80A3EC, 80A3LC and 80A3SC), possibly due to the steric hindrance in the polymer chain. Additionally, in general, increasing the hydrophobic content leads to a decrease of final molecular weight for terpolymers with larger hydrophobic chain length (compare 80A1LC with 80A3LC, 50A1SC and 50A3SC, and 80A1SC and 80A3SC), suggesting that when the hydrophobicity of the molecule is higher, this hinders the polymerization process, due to the difficulty in originating a free radical by the hydrophobic monomer, consequently inducing the finalization of polymer chains, which reduces the final molecular weight obtained. When the chain length of the hydrophobic monomer is shorter, the impact in the final polymer characteristics is less. Both these observations were previously mentioned by Lee et al.[40], in a study regarding hydrophobically modified cationic polyacrylamides for application in flocculation.

Flocculation efficiency in industrial dairy wastewater

Anionic flocculants can establish strong ionic interactions with charged moieties available on the suspended particles of the effluents. Zeta potential of the dairy effluent was assessed and values obtained are relative to the surface charge of the impurities and particles present in the effluent, which can vary according with the pH of the medium. Regarding the acidic conditions tested, for pH 3, a distribution in the zeta potential of the effluent from -40 to +15 mV was observed, with a median value of -13 mV, while for pH 5 a distribution from -32 mV to +16 mV was verified, with a median value of -7 mV. At pH 10, the closest to the initial effluent pH, the zeta potential distribution of the effluent was always in the negative range varying from -35 to -4 mV, with a median value of -19 mV, proving the stability of the original effluent, induced by the repulsion of charges. The heterogeneity of charges in the effluent was confirmed, suggesting the viability of using anionic flocculants for its treatment. The high molecular weight of the developed flocculants are also likely to promote bridging between the particle contaminants upon adsorption, thus leading to efficient aggregation of these particles, with a good propensity of the formed aggregates to settle[1].

The effectiveness of the developed polyelectrolytes as flocculants was studied based on the reduction of supernatant turbidity at different pHs and polymer dosages. Figures 4-7 show the turbidity reduction curves for pH 3, 5 and 10 for flocculant concentrations ranging from 0 to 104 mg/L. In general, for all the polymers, at pH 3 and 5 there is an increase of turbidity reduction with increasing dosage. The best results were obtained at pH 5, which coincides to the pH value at which the particles showed greatest destabilization before addition of the polymer flocculants. Polyelectrolytes from the 80 series led to better results than those of the 50 series, suggesting that higher charge density is more favorable to induce flocculation, as expected.

In most of the 80 series polyelectrolytes it was possible to achieve turbidity reductions around 90% with less than 40 mg/L of flocculant, only with the exception of the hydrophobically modified polymers using the LMA monomer (LC series). Indeed, for both the 50 and 80 series, the terpolymers with LMA were the only polymers for which the hydrophobic modification did not improve the flocculation performance, instead reducing it when compared with the corresponding copolymers. Additionally, in these cases not only the final clarification was lower, but also higher dosages were required to achieve maximum removal. This suggests that the number of methylene groups in the aliphatic chain of the hydrophobic monomer is not suitable for interactions with the oily fraction of the dairy effluent. Lee et al.[40] evaluated, in a previous study, the effect of the hydrophobic chain length in the flocculation process, and the polymer comprising a dodecyl group (12 methylene groups, similar to LMA) also presented inferior performance, requiring a higher dosage, when compared with the other hydrophobically modified polymers, comprising shorter chain lengths. The authors suggested a relation with molecular weight, which was lower for polyelectrolytes with larger hydrophobic chain lengths. In the case of the polyelectrolytes developed in the present work, some of the ones comprising LMA also present lower molecular weight values when compared with the corresponding ones comprising EA (shorter hydrophobic chain length than LMA), as already mentioned, which can explain the worse performance of the terpolymers containing LMA (see Table 3). However, when comparing with the polyelectrolytes comprising SMA (larger hydrophobic chain length than LMA), these show better performance even if they present also lower molecular weight values. As referred previously, the polyelectrolytes comprising SMA exhibit higher zeta potential values (see Table 3), as previously discussed, which can possibly explain their better performance.

For the 50 series, the presence of hydrophobicity improves the performance in flocculation in most of the cases (with exception for polyelectrolyte 50A1LC, again the polymer incorporating the LMA monomer), considering the maximum reduction of turbidity. For the 80 series, increasing the amount of the hydrophobic monomer did not show a significant effect in improving the turbidity reduction, with exception for the terpolymer 80A3SC, where the efficacy with the lower dosage (13 mg/L) increased leading to a turbidity reduction of about 88%. In addition, analysis of the results with Poly(AAm-Na-AMPS) copolymers suggests that charge density has more influence on the flocculation performance than molecular weight, for this specific effluent, since the copolymer 50AP presents a much higher molecular weight than 80AC and 80AP (see Table 3), but 80AC and 80AP show better performances. Thus, when introducing the hydrophobic monomer, performance of the 50 series is improved, in relation with the corresponding copolymer, however still not better than the performance of the 80 series copolymers, since the charge density is not high enough. In summary, the higher reductions of turbidity were achieved with the flocculants 80AC (93% turbidity reduction), 80A1EC (90%), 80A3EC (90%), 80A1SC (91%) and 80A3SC (95%), always for pH 5 and dosage of 53 mg/L.

Observing the zeta potential distribution of the effluent, mentioned previously, and comparing it with the turbidity reduction results, it is possible to see that for the pHs that show zeta potential distribution in both negative and positive regions (3 and 5), the anionic flocculants promoted reasonable or very good flocculation. However, at pH 10, which leads to a zeta potential distribution only in the negative region, and thus to a very stable effluent, very poor performances were observed. This suggests that anionic flocculants are suitable for this specific effluent, once pH is adequately adjusted. Moreover, at pH 5, the least stable effluent for the range of pHs evaluated (median zeta potential -7mv), higher turbidity removals were normally achieved.

A comparison of the turbidity reduction results here presented with reported literature reveals that much lower polymer concentration is needed in our studies, when using the novel developed polyelectrolytes, to achieve the same efficiencies[27,33]. The majority of the literature is based on inorganic coagulants, however the use of organic flocculants, even if only seldom addressed in the literature, requires lower amount of treatment agent, as was the case of the present study, which generates less volume of sludge ready for disposal after simple treatment, reducing the overall treatment cost.

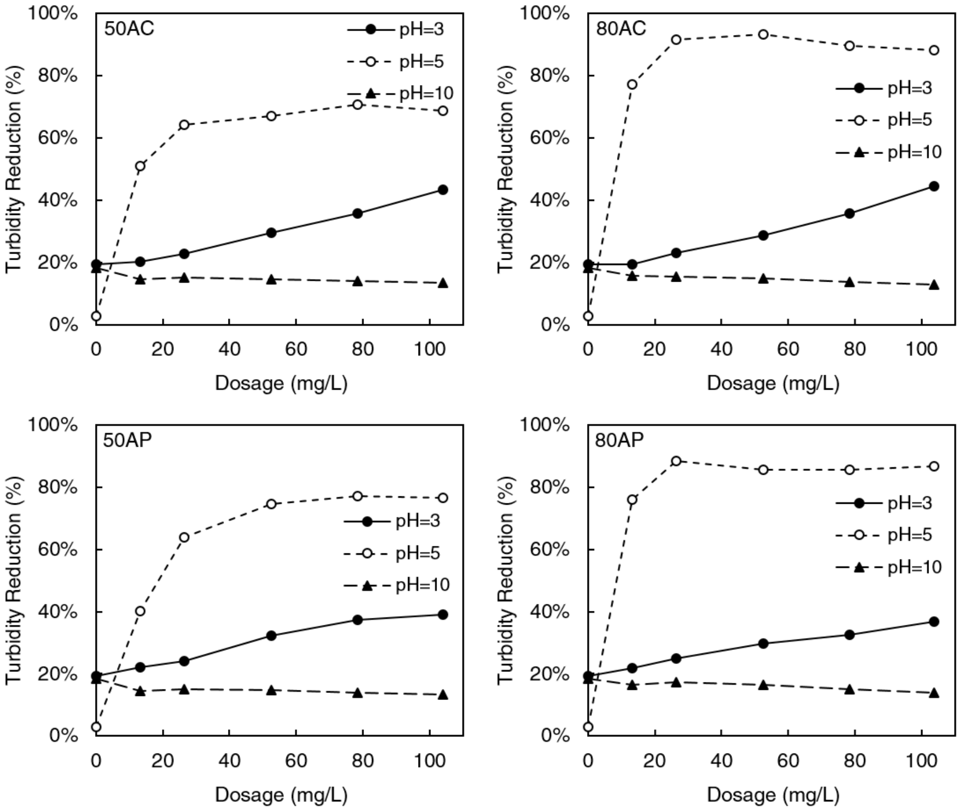

Figure 4 Turbidity reduction curves for dairy industry effluent treated by Poly(AAm-Na-AMPS): 50AC, 80AC, 50AP and 80AP, at various pH.

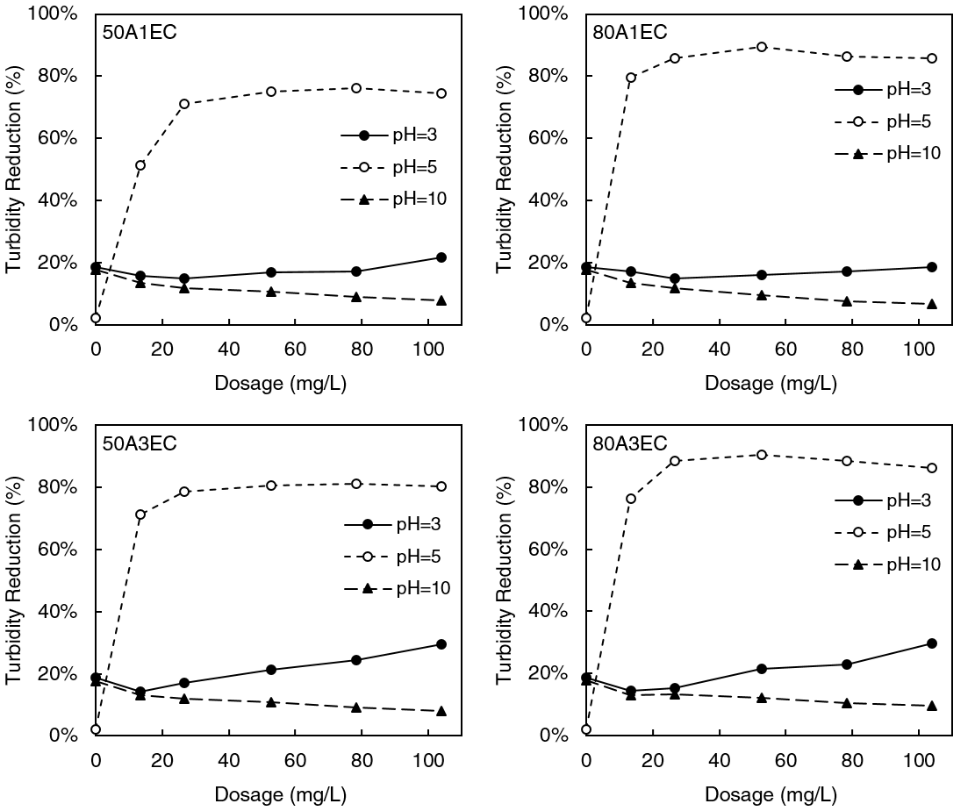

Figure 5 Turbidity reduction curves for dairy industry effluent treated by Poly(AAm-Na-AMPS-EA): 50A1EC, 50A3EC, 80A1EC and 80A3EC, at various pH.

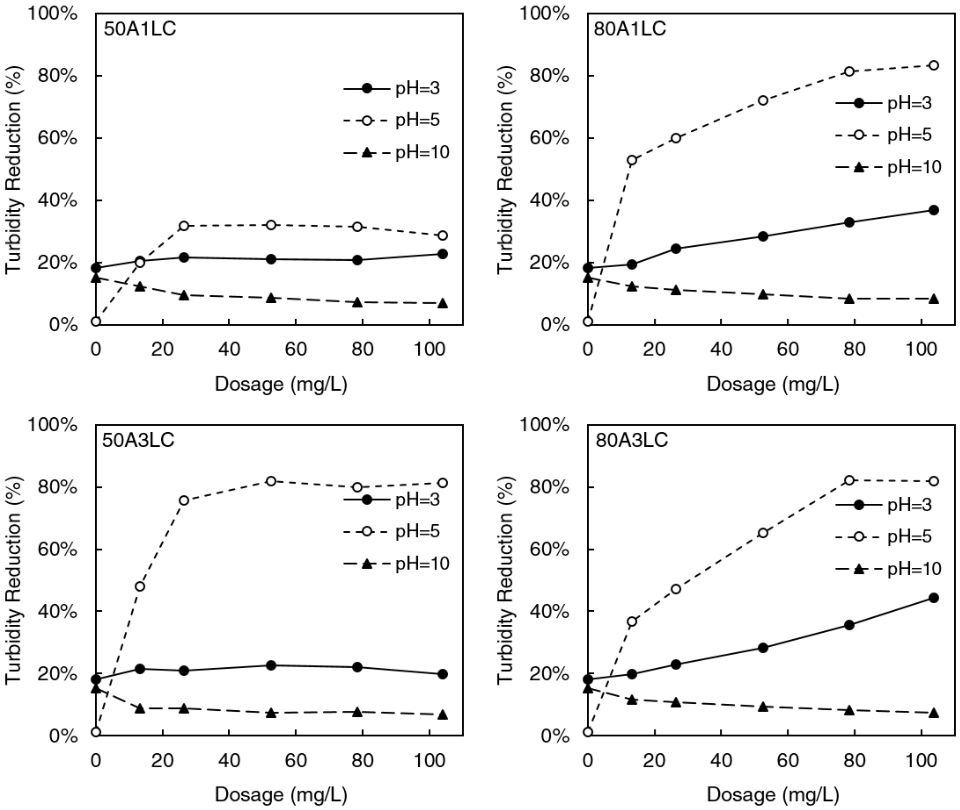

Figure 6 Turbidity reduction curves for dairy industry effluent treated by Poly(AAm-Na-AMPS-LMA): 50A1LC, 50A3LC, 80A1LC and 80A3LC, at various pH.

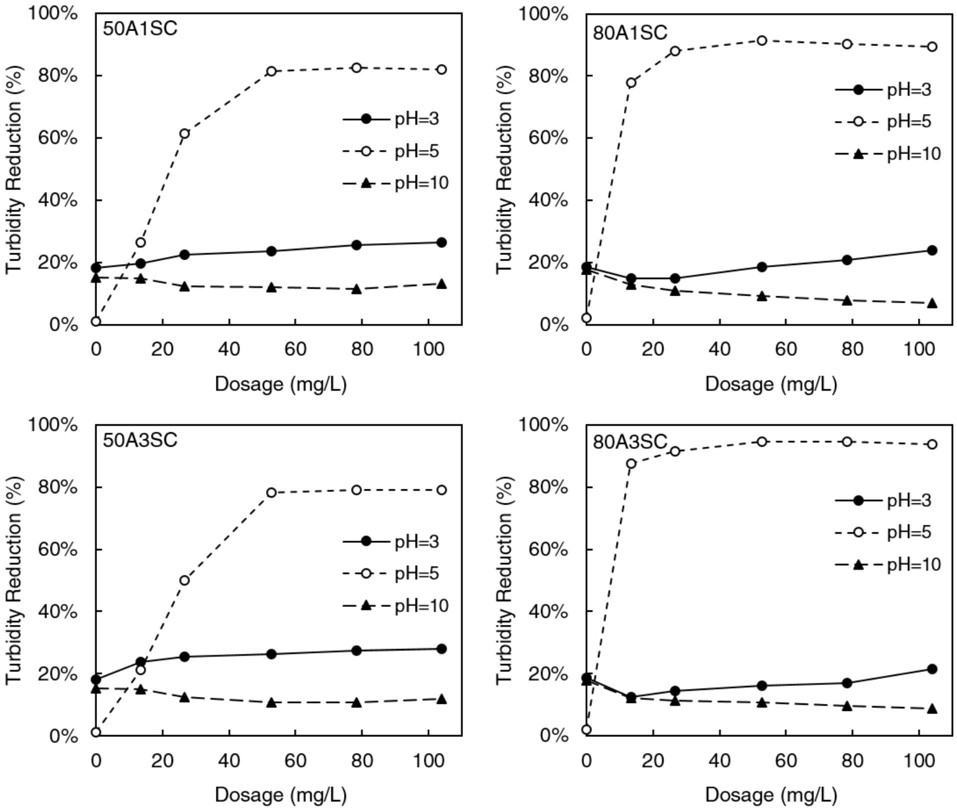

Figure 7 Turbidity reduction curves for dairy industry effluent treated by Poly(AAm-Na-AMPS-SMA): 50A1SC, 50A3SC, 80A1SC and 80A3SC, at various pH.

A commercial anionic polymer was used as reference, AlpineFloc Z1, which has similar charge density to the 50 series, in the treatment of the same effluent sample (Figure 8). At pH 3 and 10 the performance was worse than for all 50 series polymers (Figures 4 to 7). At the optimum pH of 5, it was possible to achieve above 80% turbidity reduction with 27 mg/L of AlpineFloc Z1, slightly better than with the developed polyelectrolytes with similar charge density, where the maximum of 83% was achieved only for 78 mg/L of 50A1SC. However, the highest turbidity reductions for this effluent were achieved with the polyelectrolytes with higher anionic fraction (80 series polyelectrolytes), which led to higher turbidity reductions than the reference, for lower polymer dosages.

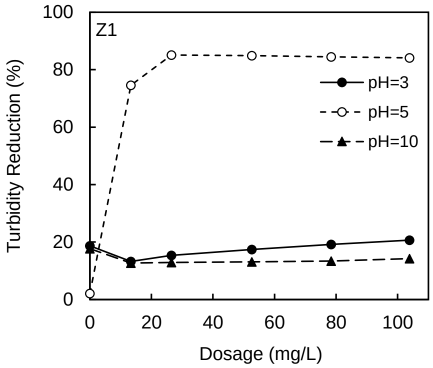

Figure 8 Turbidity reduction curves for dairy industry effluent treated by anionic reference polymer, AlpineFloc Z1, at various pH.

For the terpolymers that presented best performance in turbidity reduction, as well as for the reference polymer and the corresponding copolymer, COD and total solids removals efficiency were evaluated for optimum conditions of pH and dosage (Figure 9). The COD removal obtained was in the range of 40-45%, considerably close to the values reported in literature for similar processes[28–30,33], while total solids removal was in the range of 55-57% removal. Considering the overall results, flocculant 80A3SC seems to be the polyelectrolyte that performs the best in the treatment of dairy industry effluent (higher turbidity reduction with a low dosage (53 mg/L), and high COD and total solids removals). This polymer performed, altogether, better than the reference, for a lower dosage.

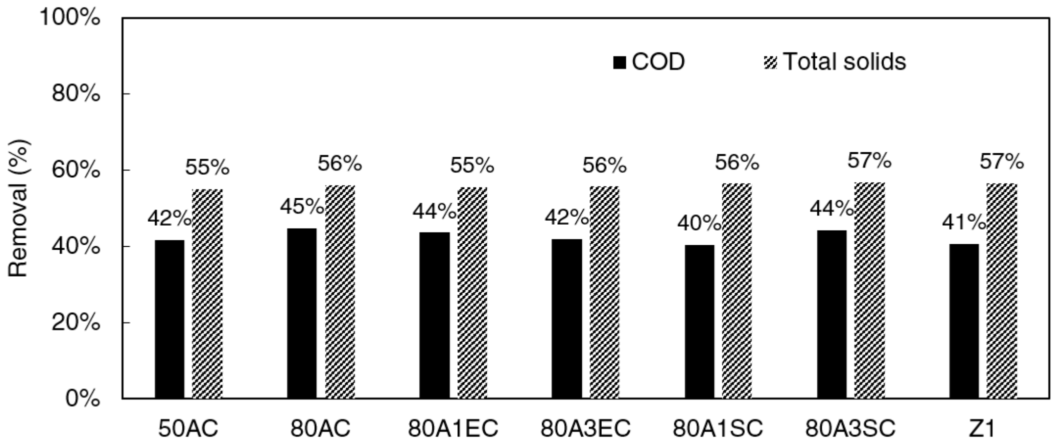

Figure 9 COD and total solids removal for treatment of dairy industry effluent with 50AC, 80AC, 80A1EC, 80A3EC, 80A1SC, 80A3SC and AlpineFloc Z1 (optimized pH (pH 5)) and for a concentration of polymer of 53 mg/L.

When the flocculation tests were performed, the first indication of flocculation were the visual observations. As soon as the lowest dosage was added, flocs formation was immediately observed. Figure 10 shows photographs of the dairy effluent before (a) and after the treatment with flocculants 80AC (b), 80A3EC (c) and 80A3SC (d) for the optimum conditions. It is possible to see a clear reduction of turbidity, as well as the presence of strong and compact flocs, which settled quickly when the mixing was stopped.

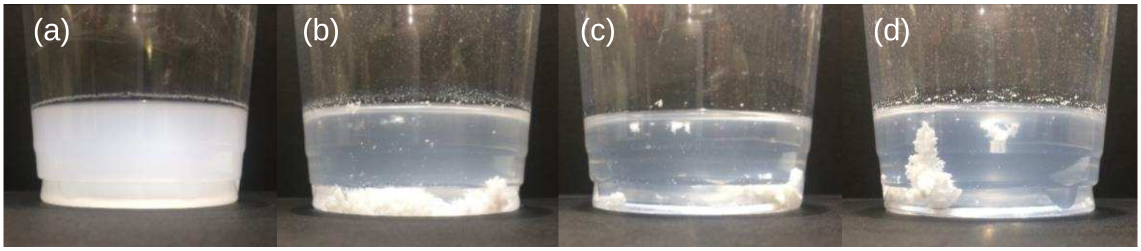

Figure 10 Initial dairy effluent (a) and effluent after treatment with flocculants 80AC (b), 80A3EC (c) and 80A3SC (d), in optimized conditions of pH (pH 5) and concentration of polymer of 53 mg/L.

CONCLUSIONS

To improve the flocculant's performance in effluents treatment, specific customized products for a target application should be developed. Additionally, to meet the present environmental requirements, these must be developed using eco-friendly approaches. Consequently, it is useful to develop treatment methodologies that combine all the environmental concerns, being efficient and cost-effective.

A range of anionic polyelectrolytes, including hydrophobically modified polyelectrolytes, was produced in the present work. Characterization of the anionic polyelectrolytes produced has shown that the formulations used in the synthesis, in the present study, which are free of aromatic compounds and metals, are suitable for the production of targeted polymers for the final application. Moreover, it was proved the ability of introducing hydrophobicity in the polymers structure and the benefits associated with this introduction.

The results obtained for the anionic flocculants applied in the flocculation of an industrial dairy effluent, indicate that polyelectrolytes with higher anionic fraction (80 series) have superior performance in the treatment process, leading to the highest turbidity reductions (above 90%), using concentrations of polymer of approximately 53 mg/L. Moreover, the best conditions of treatment suggest an ideal adjustment of the pH of the effluent to a value of 5, which destabilizes the effluent. The hydrophobic modification improved flocculation performance, especially when using the monomer with larger hydrophobic aliphatic chain (SMA), even if the corresponding copolymer (80AC) did already present very good turbidity reductions. The hydrophobic chain length also proved to have influence in the results obtained, however it was not possible to establish a direct correlation considering that this parameter also affects polymer characteristics, such as molecular weight. It is worth noting that some of the anionic flocculants developed reached turbidity reductions around 90% with concentrations around 27 mg/L and without addition of any additional aids. These polyelectrolytes revealed as well superior performance than the reference polymer tested. COD and total solids removals were also evaluated, revealing that the polyelectrolytes presented in this study led to results slightly higher than the ones presented in literature.

Future work will study the application of this type of polyelectrolytes to other oily wastewaters, namely considering possible variability in the effluents from different dairy industries.

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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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