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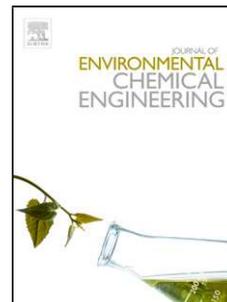


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Pre-treatment of industrial olive oil mill effluent using low dosage health-friendly cationic polyelectrolytes

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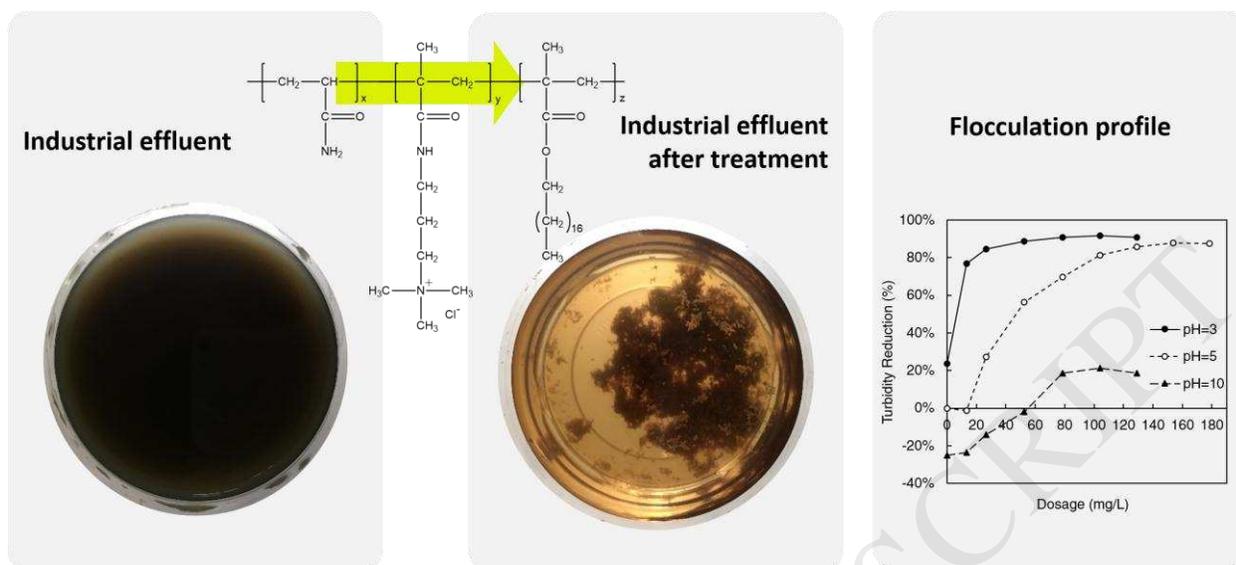
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Graphical abstract



Highlights

- Poly(AAm-MAPTAC) and Poly(AAm-MAPTAC-SMA) polyelectrolytes were synthesized and characterized.
- Their flocculation performance was evaluated in an industrial oily effluent from an olive oil mill.
- Hydrophobic modification of the polymers improved the treatment efficiency.
- Turbidity removal of 90%, COD removal of 47% and total solids removal of 34% were achieved.

Abstract

Olive oil production involves a significant annual release of industrial olive oil mill effluent (OME) to the environment. These discharges bring serious environmental problems since they are extremely hazardous for the aquatic environment due to their organic matter and high turbidity levels. The present study comprises the development of new, hydrophobically modified, cationic

flocculants directed to oily effluents application. A health-friendly formulation was used in their synthesis process, performed by inverse-emulsion. In particular, Poly(AAm-MAPTAC) was synthesized in two different polymer compositions and, as well, with the presence of a hydrophobic monomer (Poly(AAm-MAPTAC-SMA)) at several compositions up to 8 wt%. The obtained polyelectrolytes were characterized in terms of final composition, hydrodynamic diameter, zeta potential and molecular weight. Their flocculation performance was evaluated in an industrial oily effluent from an olive oil mill. Results revealed that the hydrophobic modification improves noticeably the flocculation performance of cationic polyelectrolytes in the treatment of olive oil mill effluents. In the best conditions, it was possible to achieve 90% turbidity reduction, 47% COD removal and 34% total solids removal with only 53 mg/L of flocculant. Moreover, 79% of turbidity was reduced after addition of 13 mg/L.

Keywords

Flocculation, olive oil mill effluent, wastewater treatment, polyelectrolytes

1. Introduction

Olive oil mill effluents (OME) have increased significantly in the last years as a result of the quick increasing demand for olive oil, and the existing oil extraction techniques that involve high amounts of water[1].

The composition of the produced wastewater change with climate, cultivation conditions and milling processes[2]. Typically, OME possess the following characteristics: a high concentration

of solids resulting from washing actions, an intense dark color, an acidic pH and a strong odor. These effluents, when disposed off in the environment, lead to acute problems including coloration and pollution of waters, changes in soil quality and phytotoxicity, plants growth inhibition and odor nuisance[3]. Moreover, direct discharge on fields decreases the amount of dissolved oxygen, harming aquatic fauna[4].

Therefore, OME must be treated before disposal and several treatment technologies and integrated processes have been offered to shape a suitable and effective method to deal with the produced wastewater[5]. Open evaporation ponds, or lagooning, lead to insect reproduction and increase the risk of surface and groundwater contamination[6]. Biological methods include microbiological treatment, co-digestion, aerobic and anaerobic digestion. However the OME has high concentration of fats, lipids and phenols that can compromise the growth of microorganisms and, consequently, the OME degradability[7].

Co-digestion consists in the co-treatment of one wastewater with other wastewater, which has the advantage of providing the necessary pH or nutrients level for further treatment[8,9]. The aerobic treatment stage is able to reduce the toxicity through the reduction of phenols. Several species can be used for this purpose. Hamdi *et al.*[10] and Cereti *et al.*[11] used *Aspergillus niger* and removed COD in about 52.5% and 35–64%, respectively. *Aspergillus terreus*, *Azotobacter chroococcum* and *Geotrichum candidum* were also used in different studies[12–14], and were able to reduce COD in 63.3, 74.3 and 70% and phenols in 65.6, 90 and 94.3%, respectively. Anaerobic digestion is performed by anaerobic microorganisms, generally bacteria, in the absence of molecular oxygen. This process has low energy requirements and produces low amount of sludge. Recent studies using anaerobic sludge bed reactors reported COD removals of 70-80%[15,16]. Procedure using an anaerobic sequencing batch reactor reached COD removals up to 80%[17].

Advanced oxidation processes, consisting in Fenton and Fenton-like oxidation and ozonation, can also be applied[18–20]. Physico-chemical treatment methods such as ultrafiltration, reverse osmosis, sedimentation, centrifugation, coagulation-flocculation and electro-coagulation are actually the most used methods[21–24]. Nevertheless, most of these treatment processes, on their own, are not cost effective and reported results present significant drawbacks, indicating that combined technologies are needed in order to reduce the organic load, and thus reducing the operating costs. These hybrid systems can include ozonation and aerobic biological treatment, coagulation-flocculation combined with anaerobic biological process, electron-Fenton and anaerobic digestion or chemical oxidative procedure in combination with aerobic biological treatment, among others[25,26].

In particular, coagulation-flocculation processes have proved to be very useful as a pre-treatment stage in the OME processing procedures[27,28], involving low CO₂ emissions[29]. The addition of organic and inorganic compounds stimulate the destabilization of colloidal materials and promote the agglomeration of small particles in large flocs that are able to quickly settle. Coagulants, such as alum, ferric, starch, chitosan and lime, and cationic or anionic flocculants, like poly(diallyldimethylammonium chloride) (PDADMAC), [poly(allylamine) (PAA) or poly(allylamine) hydrochloride (PAH), have been tested [23,30,31]. Experiments showed considerable reduction of solids, color and chemical oxygen demand (COD). However, usually a combination of both (inorganic and organic additives) is required or, when in single use, a very high concentration of polymer is used, which generates large amount of sludge[32]. Minimization of sludge production is important considering the costs related with consequent sludge treatment and disposal[33].

Synthesis of the aforementioned treatment products commonly comprises the presence of aromatic compounds, even at very low concentrations, that exhibit human and aquatic toxicity levels[34]. Health-friendly formulations for production of polyelectrolytes by inverse-emulsion polymerization[35] were tested and presented in a previous work [36]. The polymers are synthesized using alternative oils that are listed in the International Nomenclature for Cosmetics Ingredients (I.N.C.I.) under the designation “Paraffinum Liquidum” and comply with many pharmacopoeia and FDA regulations. The main characteristics include non-irritating, high boiling point, high stability and high purity, free of harmful ingredients, color, odor and taste. These oils have high-interest in industry, due to their physical properties and level of purity, which is required for use in personal care, food and pharmaceutical products[37].

In this work, cationic polyelectrolytes were synthesized using two different health-friendly formulations and applied as low dosage flocculation agents in the pre-treatment step for olive oil mill wastewater, and their performance was studied. The main objective of this paper was to examine the feasibility of using low dosage of high molecular weight polymers, specially designed for this type of effluents, in order to reduce the cost of the treatment. Moreover, the influence of hydrophobic content in the polymers, as well as the concentration of polyelectrolyte for different pH values were assessed. Turbidity reduction, chemical oxygen demand and total solids content were the selected criteria to screen the effectiveness of the process.

2. Materials and methods

2.1 Materials

Acrylamide solution (AAm), at 50 wt %, was purchased from Kemira (Botlek, Netherlands). The monomer [3- (Methacryloylamino) propyl] trimethyl ammonium chloride (MAPTAC) was

purchased from Qingdao Finechem Chemical Co. (Qingdao, China) and used as received. Stearyl methacrylate (SMA) was purchased from BASF (Ludwigshafen, Germany). Tert-butyl hydroperoxide (TBHP) was purchased from Acros Organics (Geel, Belgium). Meta bisulfite (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 Puresyn 4, a hydrogenated polydecene, was purchased from ExxonMobil (Switzerland). Carnation, an iso-paraffin, was purchased from Sonneborn (Amsterdam, Netherlands). Oily wastewaters tested include effluent obtained from olive oil mill (provided by Adventech Group, Portugal).

2.2 Inverse-emulsion polymerization

Inverse-emulsion polymerization was carried out in a 500 mL glass reactor. Prior to reaction, the aqueous phase was prepared with deionized water, acrylamide (AAM), [3-(Methacryloylamino) propyl] trimethyl ammonium chloride (MAPTAC) and 0.625 wt% of adipic acid for hydrolytic stability of the polymers. The copper was chelated with 334 ppm of Pentasodium DTPA. The total monomer level of the initial emulsion was 34.0 wt%. Sorbitan isostearate and PEG-7 Hydrogenated Castor Oil were the surfactants blended to obtain a hydrophilic–lipophilic balance (HLB) between 5.0 and 5.3 according with the monomers composition. Carnation and Puresyn 4 were used as organic phases. The aqueous phase was added to the organic phase under mechanical stirring for 30 min. In the case of the hydrophobically-

modified polymers (Poly(AAm-MAPTAC-SMA)), the desired amount of hydrophobic monomer, stearyl methacrylate (SMA), was added at this point to the emulsion. The monomers emulsion was then degassed with nitrogen for 60 min under mechanical stirring (700 rpm), at room temperature. Polymerizations were initiated by injecting 100 ppm of tert-butyl hydroperoxide (TBHP) aqueous solution to the reactor and then a solution of MBS 1.0 wt%. TBHP and sodium MBS were used as the initiator redox couple. The peak temperature was between 45 and 52 °C, being the exact maximum temperature of the exotherm dependent on comonomer composition. Additional quantities of TBHP and MBS were added to scavenge residual monomer. After the batch had cooled down to 32 °C, 2.20 wt% wetting agent (Synperonic LF/30) was added to allow a rapid inversion of the flocculant when added to water. A schematic representation of the synthesis reaction of the hydrophobically-modified cationic polyelectrolytes is shown in Scheme 1.

2.3 Isolation of polymers

All polymers were isolated by dilution of 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 precipitate was filtered under vacuum, washed with fresh acetone and dried in an oven at 60°C overnight. The samples were stored in a desiccator.

2.4 Polyelectrolytes characterization

FTIR spectra were recorded on a Bruker Tensor 27 spectrometer, equipped with an attenuated total reflection (ATR) MKII Golden Gate accessory with a diamond crystal 45° top plate. The

spectra were collected in the 500-4000 cm^{-1} range with a resolution of 4 cm^{-1} and a number of scans of 128. For the measurements, polymers in the powder state were used.

Charge density was determined by the colloid titration method with potassium polyvinyl sulphate (PPVS) using methylene blue as indicator, as described in the literature previously[37]. 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, static light scattering and electrophoretic light scattering, respectively, in a Malvern Zetasizer Nano ZS, model ZEN3600 (Malvern Instruments Ltd, UK). For the hydrodynamic diameter, stock solutions of 0.1 g/L for non-hydrophobically-modified polymers and 0.05 g/L for hydrophobically-modified polymers 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 °C and backscatter detection was used (173° angle), with at least three measurements for each sample performed. Molecular weight measurements of polymers were performed using stock solutions (0.5 g/L) of each polymer prepared in NaCl 0.1 M and stirred overnight. The samples for analysis were then obtained by diluting the stock solutions at several concentrations from 0.02-0.5 g/L. All samples were sonicated during 2min and passed through 0.45- μm syringe filters prior to analysis. 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, closed by cell stoppers. At least three measurements were conducted for each sample.

Table 1 summarizes the composition of the developed polyelectrolytes.

2.5 Flocculation tests

A 200-mL polymer 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 HCl or NaOH aqueous solutions, specifically 3 mL of HCl 1 mol/L were added for pH 3, and 0.2 mL and 5.5 mL of NaOH 1 mol/L were added for pH 5 and 10, respectively. Polymer solution samples with different volumes were added to the wastewater sample, with a successive increase of 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%. Solids content and chemical oxygen demand (COD) of the treated supernatant water were measured for the polymers that showed better results in turbidity reduction. A commercially available polymer flocculant provided by Aqua+Tech Specialities SA (Geneva, Switzerland) was also tested in the same conditions as a reference – this was the polymer under the commercial name AlpineFloc DHMW, a high molecular weight cationic polyacrylamide with 60 wt% charged fraction.

3. Results and discussion

3.1 Polyelectrolytes characterization

The feasibility of carrying out polymerizations in health-friendly formulations has already been studied in a previous work[36]. The choice of Carnation and Puresyn 4 as organic phases in the inverse-emulsion polymerization of these polyelectrolytes was mainly related with economic

issues. Since Carnation and Puresyn 4 led to very similar copolymer characteristics, subsequent hydrophobic modification was conducted only using the oil Carnation.

After purification of the polymers their compositions were assessed (Table 2). The amount of charged groups and the corresponding actual charge density of all synthesized polymers was evaluated by titration. For non-hydrophobic polyelectrolytes, it was observed that the amount of charged groups was slightly lower in the final polymer than the initial monomer ratios of the formulation, which can be due to both a difference in monomer reactivity ratios and a non-complete polymerization of the feed monomers. In the case of the hydrophobically-modified polyelectrolytes, it is clear that charged fraction is increased as compared to the corresponding polyelectrolytes that do not contain any hydrophobic monomers.

ATR-FTIR spectroscopy was used to characterize the copolymers for their main structural features. The spectra of the copolymers (Figure 1) showed bands at ca. 3330 cm^{-1} and 3190 cm^{-1} , attributed to the N-H stretching vibrations in the monomers. The characteristic amide I band (C=O stretching in the amide groups) of the monomers appeared as a very strong band with maximum at $1651\text{-}1660\text{ cm}^{-1}$. The frequency of this absorption maximum changed slightly between copolymer samples depending on the relative content of each monomer, i.e., acrylamide (primary amide) and MAPTAC (secondary amide) in the sample, whose amide functions absorb at a slightly different frequency. Bands showing clearly the presence of MAPTAC were observed at 1532 cm^{-1} (amide II of secondary amide), 1479 cm^{-1} (asymmetric bending of CH₃ groups), 967 cm^{-1} and 915 cm^{-1} (asymmetric stretching of C4-N bonds), with an increased intensity for the samples with a higher content of MAPTAC (60MC, 60MP, 60M1SC and 60M2SC).

It is noteworthy that FTIR spectroscopy confirmed the aforementioned results of the monomer composition in the copolymers determined by colloidal titration (Table 2), as demonstrated by the similar spectra obtained for samples 25MC and 25MP or 60MC and 60MP (of comparable monomer composition) and samples 25M1SC and 25M2SC, and samples 60M1SC and 60M2SC. Results also confirmed the reduced influence of the oil used as medium in the copolymerization reactions (similar FTIR spectra were obtained for the 25MC and 25MP samples or between the 60MC and 60MP samples, produced with different oils: MC series in Carnation and MP series in Puresyn 4).

The presence of the hydrophobic monomer used in the preparation of Poly(AAm-MAPTAC-SMA) samples was revealed by the appearance of two sharp bands in the region of the C-H stretching bands, at 2922 and 2852 cm^{-1} , which were better resolved in the spectra of 60M1SC and 60M2SC samples. These bands are due to the asymmetric and symmetric stretching of the CH_2 groups of the hydrophobic chain, respectively. Additionally, for the 60M1SC and 60M2SC samples, a band of small intensity at 1729 cm^{-1} was visible in the FTIR spectra, due to the C=O stretching in the ester bonds of the hydrophobic monomer.

A summary of the polyelectrolytes characterization, including zeta potential, hydrodynamic diameter and molecular weight is given in Table 3. The zeta potential values for the different polymers are consistent with the charge density of the polyelectrolytes evaluated by titration (Table 2). Charged groups are the crucial parameter affecting this value. Comparing the co-polymers produced in the two different formulations, it is possible to observe that polyelectrolytes synthesized using Puresyn 4 oil present higher zeta potential values, and also higher charged fraction (Table 2), when compared with polyelectrolytes synthesized using Carnation oil.

Furthermore, comparing polyelectrolytes developed using the same oil in formulation (Carnation), when hydrophobic content is present the zeta potential increases, as well as the charged fraction in the final polymer is also higher (compare 25MC with 25M1SC and 25M2SC, and 60MC with 60M1SC and 60M2SC). The hydrodynamic diameter supplies information about the polymer conformation in solution. There is a good correlation between hydrodynamic diameter and polymer molecular weight for polymers with identical charge density. Also, when charge density increases for similar molecular weight, the hydrodynamic diameter increases, as expected (compare 25M2SC and 60M2SC). Since the hydrodynamic diameters were measured in water solutions, the hydrophobicity present in the polyelectrolytes can affect their conformation in water, leading to similar diameters even when charge density increases (compare 25M2SC and 60M1SC). The molecular weight values of polymers produced are in accordance with the molecular weight range presented in the literature for polymers used in the same application[28,31].

3.2 Flocculation efficiency in an industrial effluent

The characteristics of the olive oil effluent sample used in the flocculation tests are summarized in Table 4.

Cationic flocculants have inherent positively charged groups, which are active in neutralization of negative charges on suspended colloidal particles and oil droplets during the flocculation process of oily wastewater[38]. Average-zeta potential of the suspended particles and droplets in the effluent sample was -12.6 mV, with a distribution from -25.4 to 0.9 mV, indicative of a heterogeneous effluent, confirming nonetheless the adequacy in the use of cationic flocculants. Also, long polymer chains with medium charge density can promote the bridging effect between

the particles, due to the polymer adsorption on the particle surface in a way that is extended and can interact with other particles[39–41].

The influence of pH and dosage of each flocculant was evaluated. Herein, the supernatant water turbidity was used to evaluate the oil removal efficiency. Figures 2 and 3 show the effect of pH on polyelectrolytes performance in OME treatment at different concentrations from 0-180 mg/L, until the turbidity reduction reaches a stable value, for the different polyelectrolytes produced. As can be seen, with increasing dosage, gradual increase was observed in the reduction of turbidity. Acidic conditions always appear to lead to higher removal efficiencies, and the addition of focculant did not change the effluent pH. Furthermore, adjustment of the effluent to pH 3 decreased, by itself, the turbidity in about 20%. At pH 3, turbidity reduction was at the highest level for all the polymers tested, and was almost complete for dosages above 80 mg/L for all polyelectrolytes with the highest charge density (60 series). When these four flocculants were used for different pHs, the wastewater needed much higher concentrations of polymer to reduce turbidity. Moreover, adjusting pH to basic conditions increased the turbidity of the initial wastewater by itself, severely reducing the flocculant efficiency.

When the charge density is lower, the concentration of polymer required to achieve the same turbidity reduction is higher. This may be attributed to the fact that lower cationic charge density is less effective in neutralizing the negative charge on the oil droplets. Besides the charge density, these polymers present a higher hydrodynamic diameter, favoring, also, the bridging mechanism.

When the hydrophobic monomer is introduced in the polymer chain, higher levels of oil removal were achieved with lower polymer dosages. In addition, better performance is obtained for the higher charge densities. When the amount of the hydrophobic monomer increased, the

performance of the polymer improved slightly, a lower dosage of flocculant being required for the same removal efficiency, particularly in the case of the higher charge density polymers.

The use of either Carnation, iso-paraffin, or Puresyn 4, hydrogenated polydecene, in the synthesis process did not affect the performance of the polyelectrolytes (compare the graphs for the MC and MP series of polymers), which is consistent with the similarity of the characterization parameters (zeta potential, hydrodynamic diameter and molecular weight) for these two types of polyelectrolytes for similar amounts of the cationic monomer (see Table 2). A more structural analysis regarding the influence of the organic phases used has already been presented in a previous study[36].

Considering that molecular weight of the higher charge density hydrophobically-modified polymers is lower, improvement of performance must be justified by the affinity between the hydrophobic part of the polymer and the oil droplets in the effluent. Previously Lü *et al.*[42] and Bratskaya *et al.*[43] demonstrated that oil removal efficiency was significantly enhanced using hydrophobically-modified cationic flocculants.

The performance of the new polyelectrolytes developed in this study was compared with the reference polymer (Figure 4) commercially available from Aqua+Tech. AlpineFloc DHMW, which has a similar charge density to the 60 series in this work. Looking at the results for pH 3, which provided the highest oil removal efficiency, the reference polymer showed a similar behavior as the newly developed copolymer with analogous charge density. Nevertheless, 60MC and 60MP achieved higher turbidity reduction values than DHMW when comparing the same dosages. When comparing the performance of the hydrophobically-modified polyelectrolytes

developed (25M1SC, 25M2SC, 60M1SC and 60M2SC) with this reference commercial polymer, the former show a much higher removal efficiency. This evidence proves once again that addition of a hydrophobic monomer to the copolymers highly improves the flocculation performance of cationic polyelectrolytes in the treatment of industrial olive oil mill effluents.

Additionally, it must also be stressed the new polymers developed present always better performance than the reference commercial polymer when testing at all other pHs, particularly for pH 5. In fact, the commercial flocculant shows almost zero removal for these pH values.

The total solids and COD removal efficiencies were measured (figure 5) for the polymers that presented higher turbidity reduction and in the optimized conditions of pH and concentration, in order to confirm that pre-treatment was also efficient regarding these two parameters. For both parameters, the removal for the different polymers tested was very similar with a slightly better performance of the polyelectrolyte 60M1SC. Comparing these results with previous publications for coagulation/flocculation of olive oil mill effluents, the removal range is similar, however much lower dosage was needed to reach a similar effect. In Sarika *et al.*[44], four cationic and two anionic polyelectrolytes were tested in direct flocculation and shown to be capable to remove nearly completely TSS and reduce considerably COD (55%) with a minimum dosage of about 2500-3000 mg/L, is the best cases. Michael *et al.*[45] studied coagulation/flocculation as pre-treatment in the application of a solar-driven advanced oxidation process (solar Fenton), using ferrous sulfate (FeSO_4) (6670 mg/L) as the coagulant, and an anionic polyelectrolyte (287 mg/L) as flocculant, leading to approximately 44% of COD removal and TSS was removed by 94%, in line with the results obtained in the present work, for COD removal. Rizzo *et al.*[30] investigated

the coagulation of olive mill wastewater by natural organic coagulants, as possible alternative to conventional metal based coagulants. Chitosan was chosen and provided high performances in terms of turbidity (94%) and TSS (81%) removals under an optimized dosage of 400 mg/L.

The digital micrographs displayed in figure 6 show the flocs structure after addition of the suitable dosage of 60MC (b), 60MP (c), 60M1SC (d) and 60M2SC (e) to the initial effluent sample (a), at pH 3. Flocs resulting from the flocculation with the new developed polyelectrolytes had very fast growing and settling performance, presenting a high resistance to breaking actions and strong and compact structure after formation, suggesting a low water content in the flocculated fraction.

4. Conclusions

Direct-flocculation is a simple and easily applicable method for treatment of wastewaters. The health-friendly formulations used in the development of the flocculation agents, presented in this work, led to polyelectrolytes with suitable characteristics for the final application. The characterization of the polyelectrolytes produced proved the success of the hydrophobic content integration, without affecting the factors that have the main influence in the flocculation process, like zeta potential or molecular weight.

The cationic polyelectrolytes produced revealed to be very promising as pre-treatment agents for treatment of olive oil mill effluents. Moreover, the hydrophobic modification of the polymers

improves the treatment efficiency, reducing, simultaneously, the associated treatment cost, since lower dosages are needed to reach the same treatment effectiveness.

The application of hydrophobically-modified polyelectrolytes, with 41-47 wt% of charged fraction, in dosages around 53 mg/L, were the most effective in the flocculation process. Turbidity removal of 90%, COD removal of 47% and total solids removal of 34% were achieved. Furthermore, encouraging results were obtained after addition of only 13 mg/L of flocculant, with reduction of turbidity around 79%.

In summary, the polyelectrolytes developed for direct flocculation proved to be an effective pre-treatment solution for the harsh effluent targeted (olive oil mill effluent), considering the different parameters usually analyzed, and also a more economic method when compared with alternative/standard coagulation-flocculation procedures which use larger amounts of flocculant and generate high volumes of sludge, expensive to treat

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Figures

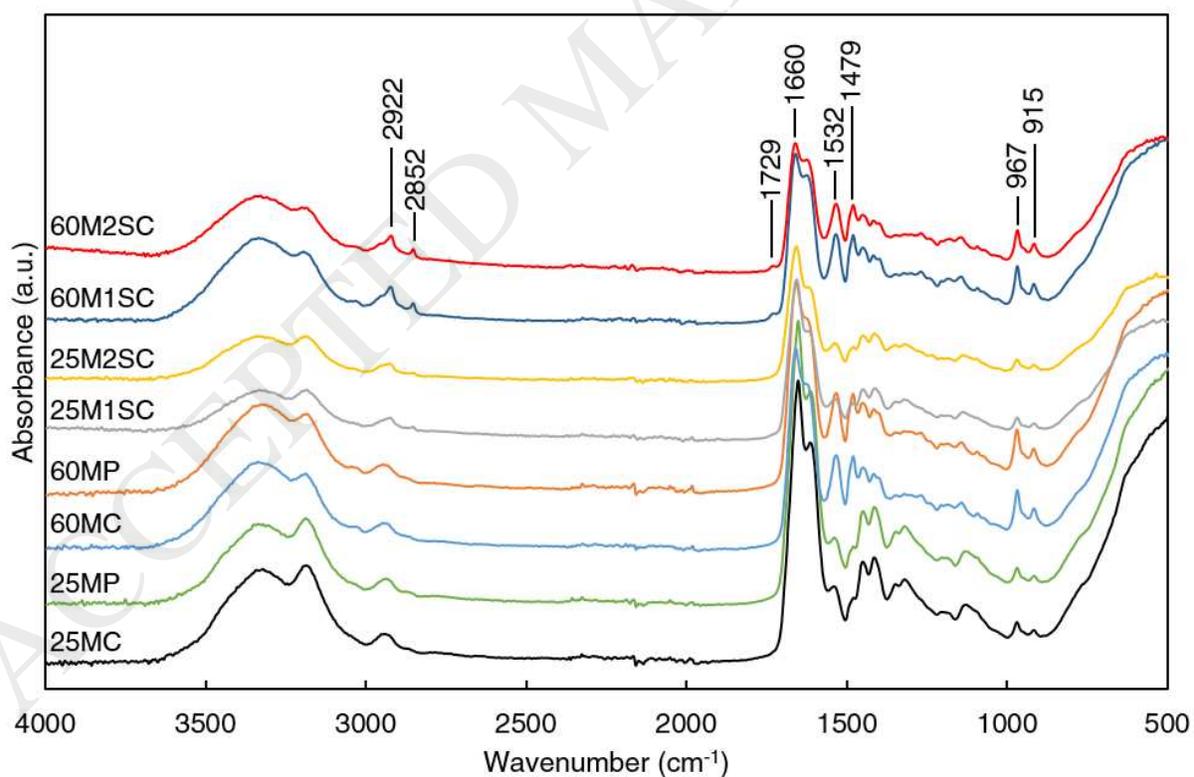


Figure 1. ATR-FTIR spectra for the polyelectrolytes prepared. Poly(AAm-MAPTAC): 25MC, 25MP, 60MC and 60MP. Poly(AAm-MAPTAC-SMA): 25M1SC, 25M2SC, 60M1SC and 60M2SC.

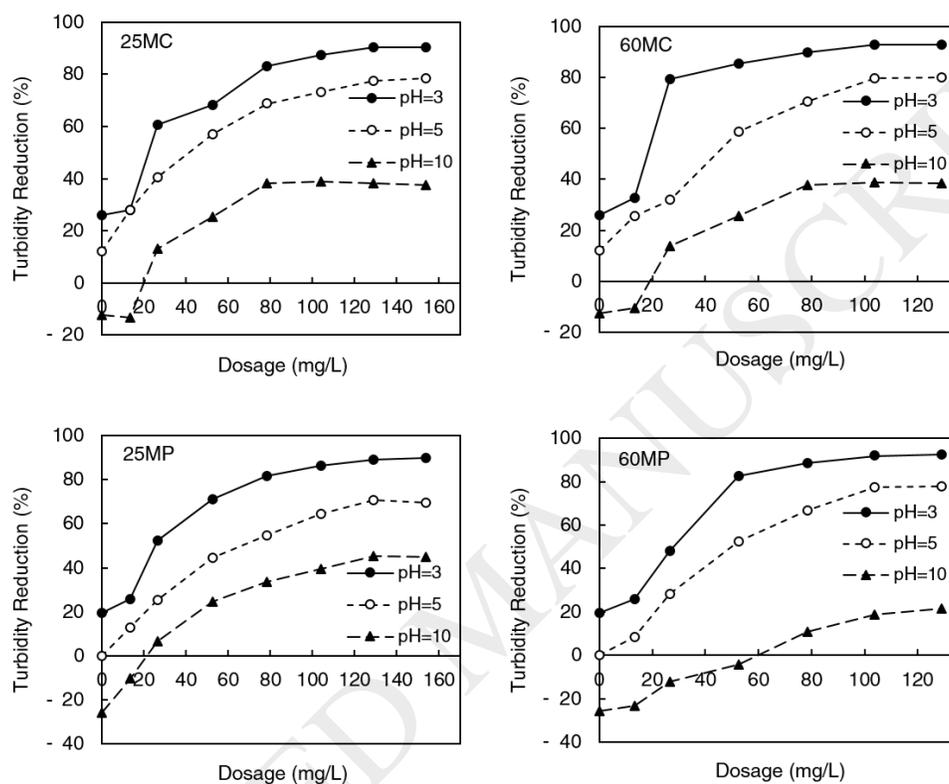


Figure 2. Turbidity reduction curves for the industrial olive oil mill effluent treated by polyelectrolytes Poly(AAm-MAPTAC): 25MC, 25MP, 60MC and 60MP, at three different pHs.

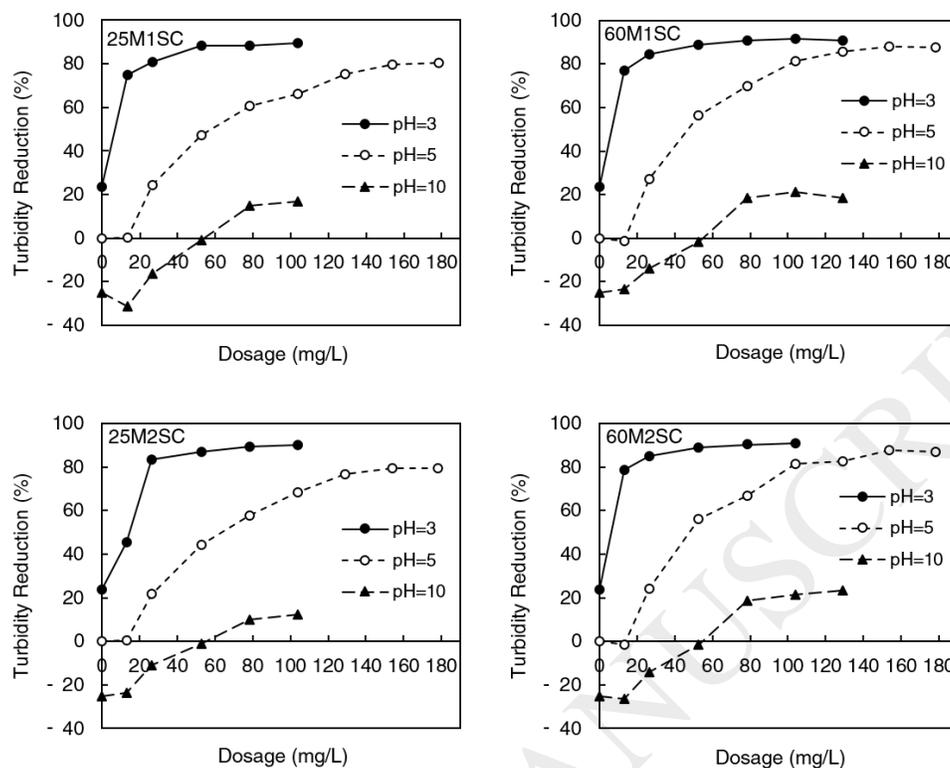


Figure 3. Turbidity reduction curves for the industrial olive oil mill effluent treated by polyelectrolytes Poly(AAm-MAPTAC-SMA): 25M1SC, 25M2SC, 60M1SC and 60M2SC, at three different pHs.

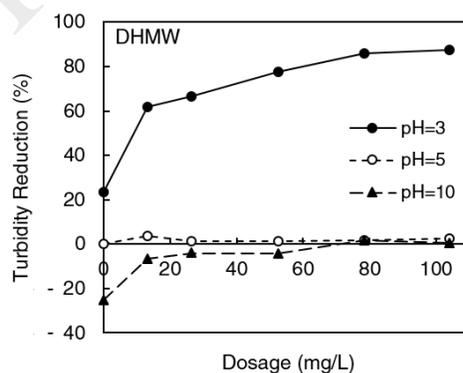


Figure 4. Turbidity reduction curves for the industrial olive oil mill effluent treated by reference polymer, AplineFloc DHMW, at various pHs.

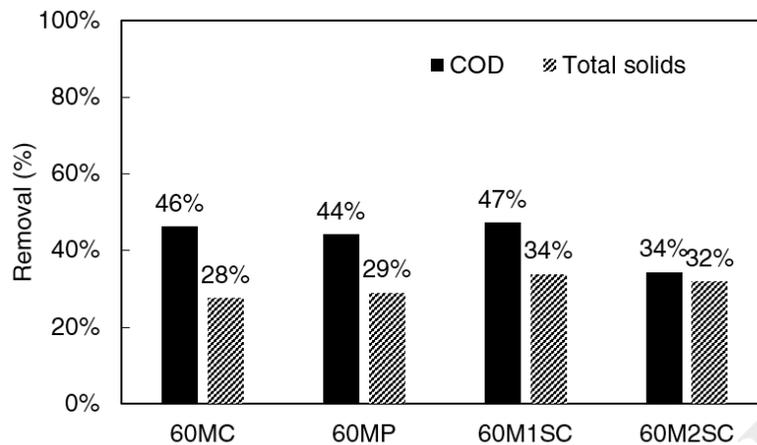


Figure 5. COD and total solids removal after the treatment of the industrial olive oil mill effluent with 60MC, 60MP, 60M1SC and 60M2SC flocculants, in optimized conditions of pH and concentration.

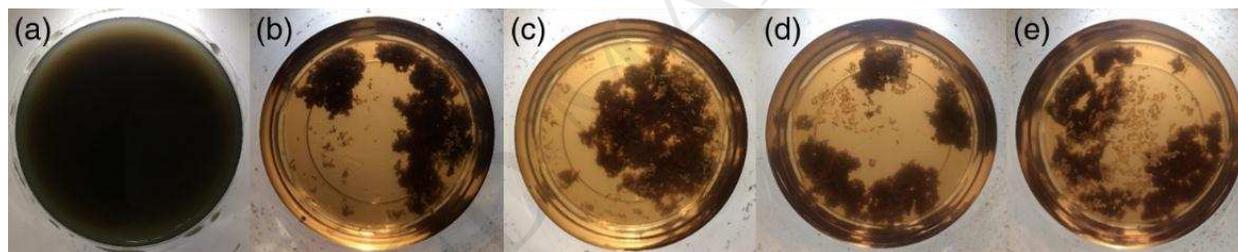
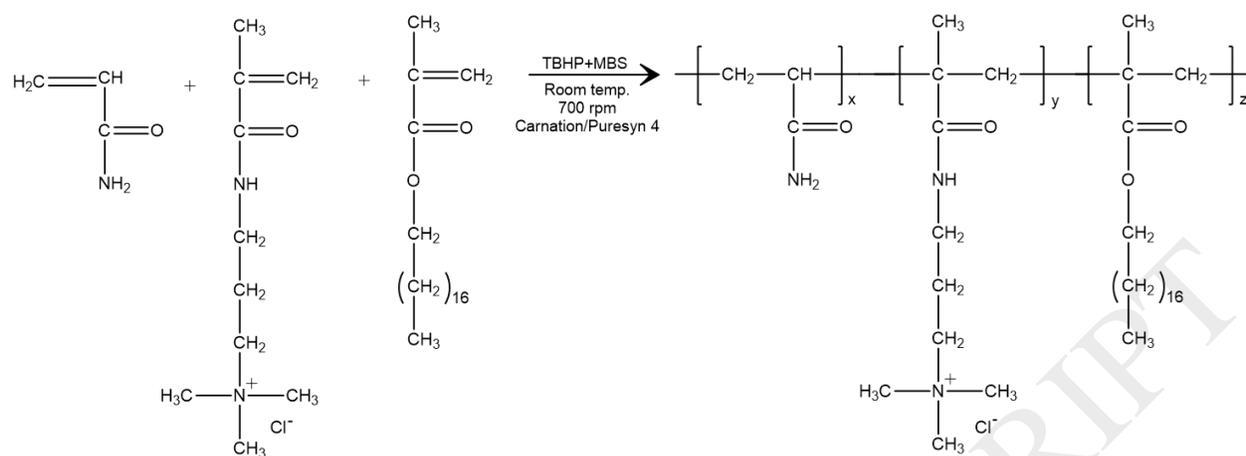


Figure 6. Initial effluent (a) and effluent after treatment with flocculants 60MC (b), 60MP (c), 60M1SC (d), and 60M2SC (e), in optimized conditions of pH and concentration.



Scheme 1. Representation of the synthesis reaction for Poly(AAm-MAPTAC-SMA), using monomers of acrylamide, MAPTAC and stearyl methacrylate.

Table 1. Summary of the polyelectrolytes initial composition at the beginning of the polymerization. Poly(AAm-MAPTAC): 25MC, 25MP, 60MC and 60MP. Poly(AAm-MAPTAC-SMA): 25M1SC, 25M2SC, 60M1SC and 60M2SC.

Copolymer designation	Monomer 1	Ratio (wt%)	Ratio (mol%)	Monomer 2	Ratio (wt%)	Ratio (mol%)	Monomer 3	Ratio (wt%)	Ratio (mol%)	Organic phase
25MC	AAm	75	90	MAPTAC	25	10				Carnation
60MC	AAm	40	67	MAPTAC	60	33				Carnation
25MP	AAm	75	90	MAPTAC	25	10				Puresyn 4
60MP	AAm	40	67	MAPTAC	60	33				Puresyn 4
25M1SC	AAm	73	90	MAPTAC	23	9	SMA	4	1	Carnation
25M2SC	AAm	71	89	MAPTAC	21	9	SMA	8	2	Carnation
60M1SC	AAm	38.5	67	MAPTAC	58.5	32	SMA	3	1	Carnation
60M2SC	AAm	37	66	MAPTAC	57	32	SMA	6	2	Carnation

Table 2. Charged fractions calculated from the initial mass balance and estimated by titration.

Poly(AAm-MAPTAC): 25MC, 25MP, 60MC and 60MP. Poly(AAm-MAPTAC-SMA): 25M1SC, 25M2SC, 60M1SC and 60M2SC.

Copolymer	Charged fraction from the initial mass balance (wt%)	Charged fraction estimated from titration method (wt%)
25MC	25	22.7 ± 0.8
60MC	60	41.5 ± 2.2
25MP	25	23.4 ± 0.7
60MP	60	42.9 ± 0.2
25M1SC	23	29.3 ± 0.1
25M2SC	21	28.2 ± 0.1
60M1SC	58.5	46.7 ± 0.2
60M2SC	57	45.6 ± 0.2

Table 3. Polyelectrolytes characterization: zeta potential, hydrodynamic diameter and molecular weight. Poly(AAm-MAPTAC): 25MC, 25MP, 60MC and 60MP. Poly(AAm-MAPTAC-SMA): 25M1SC, 25M2SC, 60M1SC and 60M2SC.

Copolymer	Zeta Potential (mV)	Hydrodynamic diameter (nm)	Molecular weight (10 ⁶ Da)
25MC	44 ± 2	70 ± 2	0.5 ± 0.02
60MC	75 ± 1	234 ± 9	2.9 ± 0.7
25MP	66 ± 1	51 ± 2	0.4 ± 0.04
60MP	79 ± 2	287 ± 13	3.1 ± 0.03
25M1SC	61 ± 1	101 ± 5	1.1 ± 0.03
25M2SC	62 ± 1	138 ± 1	1.1 ± 0.2
60M1SC	97 ± 1	138 ± 9	1.0 ± 0.09
60M2SC	89 ± 1	159 ± 7	1.3 ± 0.01

Table 4. Characteristics of the industrial olive oil mill effluent.

Parameter	Values
pH	4.7
COD (gO ₂ /L)	11.8
Total solids (g/L)	5.99
Turbidity (NTU)	3440
Colour	Dark brown

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