Effect of aluminum sulfate and cationic polyelectrolytes on the destabilization of emulsified wastes

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Abstract

Emulsified oil in wastewater constitutes a severe problem in the different treatment stages. Aluminum salts have been traditionally used as coagulants in wastewater treatments. Polyelectrolytes are used to coagulate and flocculate colloidal systems. The performance of aluminum sulfate in comparison to polyelectrolytes (chitosan and polyacrylamide) as conditioning chemicals for an emulsion waste was tested, and the predominant mechanisms acting in each case were analyzed. Turbidimetry, jar test, colloidal titration and microscopy were used to test emulsion destabilization. Both charge neutralization and bridge formation were identified and confirmed as mechanisms of interaction of polyelectrolytes with waste constitutents. Charge neutralization would be more important for chitosan than for polyacrylamide treatment. A coincidence between the doses necessary to reach zero colloidal charge and minimum turbidity was observed for polyelectrolytes. The time necessary to produce system clarification was larger for aluminum sulfate than for polyelectrolytes; this time was shortened for higher aluminum sulfate concentration. The pH showed a marked effect on aluminum sulfate performance with the optimum at pH 6; polyelectrolyte action was practically not affected by pH. Polyelectrolyte addition produced the minimum turbidity for the same doses that zero colloidal charge; at higher doses, emulsion was restabilized and became turbid again. However, aluminum sulfate treatment did not produce emulsion restabilization. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Emulsions; Aluminum sulfate; Chitosan; Polyacrylamide; Flocculation

1. Introduction

Food-processing plants generally discharge large volumes of wastewater. Reducing environmental loading from food processing wastes, decreasing processing costs and developing new food and other products which utilize residues are strong motivations for waste treatments. Emulsified oil in wastewaters can lead to severe problems in the different treatment stages. Oil in wastewaters has to be removed in order to: (1) prevent interference in water treatment units; (2) reduce fouling in process equipment; (3) avoid problems in the biological treatment stages; and (4) comply with water discharge requirements.

Aluminum salts have been traditionally used as coagulants for wastewater treatments and to remove phosphates and color. Unfortunately, Al^{+3} chemistry is extremely complex [1]. These compounds undergo a series of hydrolysis reactions; the water molecules that participate of the ionic hydration sphere are progressively replaced by hydroxyl groups [2]. Significant amounts of non-hydrolyzed Al^{+3} can only be found under low pH. The small size of Al^{+3} and consequently, its hydrophilic character maintains six water molecules octahedrally oriented around Al^{+3} ion [3]. Aluminum hydroxide precipitates at alkaline pH after hydrolysis. Further increase of pH solubilizes the precipitate by $Al(OH)_4^-$ formation. Actually, a series of multinuclear species like $Al_2(OH)_2^{4+}$ and $Al_{13}(OH)_{34}^{5+}$ are formed as hydrolysis products. Minimum solubility of Al^{+3} is reached at pH 6.5 and hydrolysis precipitation occurs in a narrow pH.

Natural and synthetic polyelectrolytes such as chitosan and polyacrylamide are typical polymeric flocculants. Polyelectrolytes with molecular weights lower than 10^6 are not usually effective.

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Chitosan is a high molecular weight carbohydrate polymer manufactured from chitin. It is a natural cationic polyelectrolyte formed by N-acetyl-D-glucosamine units with β (1–4) glycosidic bounds [4]. The cationic nature of chitosan is owed to the free amino groups left by partial removal of acetyl groups of chitin [5]. Chitosan is a linear polyelectrolyte at acidic pH. It has a high charge density, one charge per each glucosamine unit. Since many materials carry negative charge, the positive charge of chitosan interacts strongly with negative surfaces to give an electric neutrality [6].

Acrylamide is a crystalline, relatively stable monomer that is soluble in water and many organic solvents. It undergoes polymerization by conventional free-radical methods, but can also be polymerized photochemically [7]. All current industrial production is believed to be through free-radical polymerization. The pH of the reaction medium is also important, since hydrolysis of amide groups occur at high pH, whereas imidization is favored at low pH and high temperature. Industrial processes utilize free-radical methods of polymerization to produce a variety of polymers differing in molecular weight (from ca. 2×10^5 to ca. 1×10^7) and composition. By far the greatest current interest is in those polymers having very high molecular weights ($> 5 \times 10^6$).

In certain circumstances, the particles of a dispersion may adhere to one another and form aggregates of successively increasing size which may, despite the tendency of thermal motion to keep them in suspension, separate out under the influence of gravity. The nature of the aggregated material may depend on the conditions of its formation, or it may change with time.

The objectives of the present work were: (1) to compare the performance of aluminum sulfate and natural and synthetic polyelectrolytes (chitosan and polyacrylamide) as conditioning chemicals for emulsion waste and to analyze the effects of the dose, on emulsion restabilization and colloidal charge; (2) to determine the influence of the various factors such as ionic strength and pH on the conditioning dose and on the time to achieve minimum turbidity; and (3) to establish the predominant action mechanism in each case.

2. Materials and methods

The model system of the waste consisted of sunflower oil/water emulsions with variable ionic strength (different NaCl concentration). Oil concentration in the emulsions were studied in two levels 1.33 and 5 g/l. An ionic emulsificant (sodium dodecyl sulfate, SDS) was added to each sample to inhibit coalescence of the oil droplets; the molecular weight of SDS is 288.36. The presence of SDS produced negatively charged emulsions; two concentrations of SDS were analyzed 0.2 and 0.05 g/l. The emulsions were prepared in a colloidal mill

(AD-35 R Colmil, Argentina), at maximum speed with a stirring time of 15 min. Stability of the emulsions was analyzed by micrographs over 3 days storage time. Sizes of emulsion drops were measured and distribution frequencies were determined.

Three destabilizers were tested as coagulating and flocculating agents: aluminum sulfate (Anedra), chitosan a natural cationic polyelectrolyte (Sigma, practical grade obtained from crab shells with a degree of deacetylation of 77%), and a cationic polyacrylamide of high molecular weight (MW 4.10^6, Cytec Argentina S.A.) were used. Aluminum sulfate was dissolved in distilled water (10 g/l). Chitosan solutions (5 g/l) were prepared by dissolving chitosan in 1% (v/v) acetic acid solution during continuous agitation for several hours, followed by a vacuum filtration to eliminate insolubles [8]. Cationic polyacrylamide (1 g/l) was prepared by dissolving the polyacrylamide in distilled water.

To study the ionic strength effect, NaCl concentrations varied from 10^{-3} to 10^{-1} mol/l. The performance of destabilizers was tested in terms of the doses and the time necessary to reach minimum turbidity in the system. The ratio between surfactant concentration to sunflower oil concentration was also changed; the pH of the system ranged from 4 to 8 by adding either NaOH or HCl.

Flocculation experiments were carried out by adding the desired amount of the tested destabilizers to the emulsion with continuous agitation by a magnetic stirrer (IKA Labortechnic, IKAMAG RCT basic, Germany). To analyze the flocculation process different techniques were used: colloid titration, jar test, turbidimetric method and microscopy observation.

Turbidity was measured with a La Motte Turbidimeter, 2008 model, Chestertown, MD, USA and pH was measured with an electronic pHmeter Hach, EC30 Benchtop Model 50100, Loveland, CO, USA.

Colloid titration was used to determine the colloidal charge and the isoelectric point of the system (emulsions with a negative charge) [9,10]. A known excess amount of methyl glycol chitosan (MGC) was added in each test. MGC is a cationic polysaccharide which acts as a positively charged titrant over the entire pH range. The oppositely charged colloids react almost stoichiometrically, neutralizing the charge of the system. The remaining excess of MGC is back-titrated by potassium polyvinyl alcohol sulfate (PVSK) using toluidine blue (TB) as an indicator. PVSK has $-SO_4H$ functional groups which are ionized to $-SO_4^-$, with the production of a negative colloid. When TB solution is mixed with a positive colloid, the color of the resulting suspension is light blue. However, when TB solution is added to a suspension of a negative colloid, the resulting mixture has a purple color [9].

MGC solution was prepared by dissolving 0.2094 g MGC Sigma (product number M3150) in 1 l distilled

water. PVSK solution was prepared by dissolving 0.081 g potassium polyvinyl sulfate Sigma (product number P6000) in distilled water to make 1 l. The solution of TB was obtained by dissolving 0.1 g toluidine blue Sigma (product number T3260) in 100 ml distilled water. MGC and TB were added to emulsion samples during agitation on a magnetic stirrer; titration was carried out with 10^{-5} eq/l PVSK.

Microscopy observations were done on the emulsions and on the flocs with a Leitz Ortholux II microscope having a built-in-camera (Leitz, Germany). To obtain micrographs a shutter speed of 1/1000 s and fast film (ASA 400) were used to avoid microscale movements and distortion effect in the sample. Micrographs were digitized to measure droplet sizes with an image analyzer software. Enough micrographs were analyzed to assure statistical validity of the droplet sizes informed [11].

Flocculation assays were performed using the jar test (Decalab, Argentina) with six stirrers having a maximum speed of 250 rpm. Different amounts of polyelectrolyte were added to 500 ml aliquots. Samples were stirred at high speed for 3 min and then at 50 rpm for 10 min.

2.1. Statistical analysis

Assays were performed in duplicate and analyses of all samples were performed in duplicate and averaged. Statistical analyses were done using a computer system package (SYSTAT Inc., 1990, version 5.0). Analyses of variance were performed by ANOVA procedures. Significant differences between means were determined by LSD test; significance of differences were defined at $P < 0.05$.

3. Results and discussions

3.1. Effect of the conditioning agent dose on emulsion restabilization

Stability of the emulsions was tested over a 3-day storage period. Non-significant differences were observed in the mean droplet sizes of the emulsion with time; emulsions were maintained stable over this period. Fig. 1a and b shows colloidal charge and turbidity values as a function of aluminum sulfate dose for an emulsion formulated with 5 g/l and 0.2 g/l SDS. In the aluminum sulfate treatment, once the emulsions were destabilized and reached the lowest turbidity values (optimum dose), further addition of aluminum sulfate did not restabilize the emulsions and turbidity remained low (Fig. 1b). Since the doses used were above the solubility limit, aluminum hydroxide precipitated rapidly and the formation of soluble intermediates were not detected; in
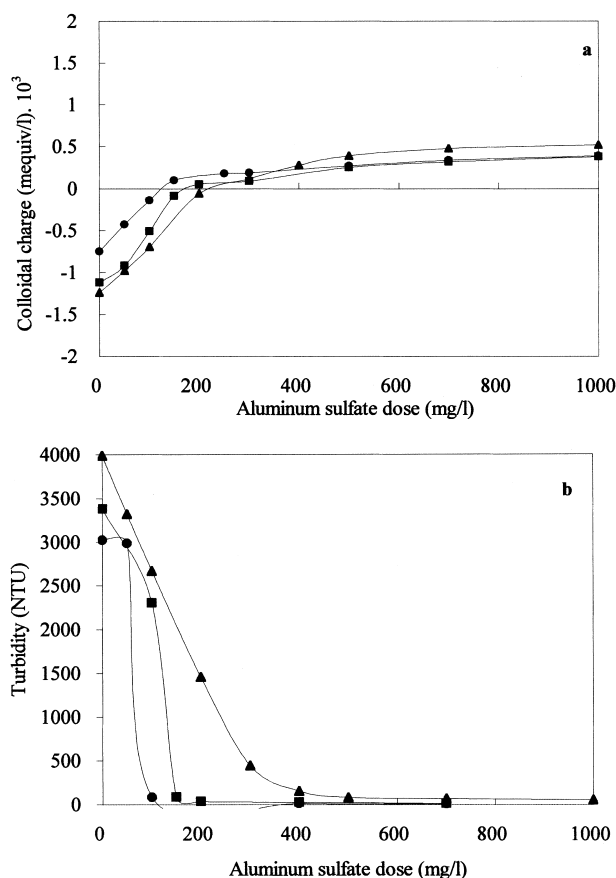

Fig. 1. (a) Colloidal charge and (b) turbidity as a function of aluminum sulfate dose for emulsions formulated with 5 g/l oil and 0.2 g/l sodium dodecyl sulfate containing (▲) NaCl 10^{-3}, (■) 10^{-2} or (●) 10^{-1} mol/l.

this case restabilization could be delayed or even eliminated [3]. Changes in the sign of the colloidal charge were observed as aluminum sulfate dose increased (Fig. 1a).

In polyelectrolyte treatments (polyacrylamide or chitosan), as long as colloidal charge was maintained around zero, turbidity also showed low values. However, when the applied dose was higher than the optimum, colloidal charge and turbidity both increased showing emulsion restabilization (Fig. 2).

Several workers [12,13] have observed restabilization of the colloidal suspensions due to excessive treatment with polyelectrolytes. Charge reversal cannot be explained by the Gouy-Chapman model for the double layer because purely coulombic attraction will not permit an attraction of counter-ions in excess of the original surface charge of the colloid. It is therefore necessary to consider additional energy terms arising from specific chemical interactions in order to explain this phenomenon [14].

Doses to reverse colloidal charge were higher for aluminum sulfate than for polyacrylamide; the lower doses corresponded to chitosan treatment. These results can
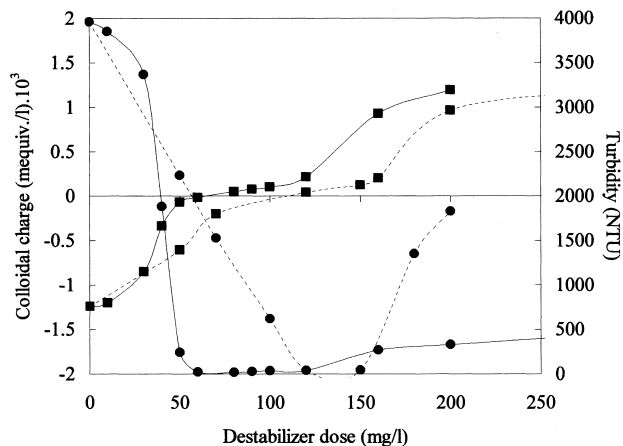
Fig. 2. (■) Colloidal charge and (●) turbidity as a function of destabilizer dose: chitosan (—) and polyacrylamide (- - -), for emulsions formulated with 5 g/l oil, 0.2 g/l sodium dodecyl sulfate and 10^{-3} mol/l NaCl.

be explained on the basis of the higher charge density of chitosan, requiring lower doses to destabilize the emulsion. Differences in charge density between chitosan and polyacrylamide were detected by the titration of their electrical charge with potassium polyvinyl sulfate; results showed that charge density ratio between chitosan and polyacrylamide was 1.64.

Non-significant differences between the doses to reach zero colloidal charge and those to reach minimum turbidity (optimum dose) were found for both polyelectrolytes. These results were not found in aluminum sulfate treatments.

In all treatments, when NaCl concentration increased (higher ionic strength), the dose of destabilizer necessary to reach zero colloidal charge decreased (Table 1). An increase of neutral salt concentration decreases the thickness of the double layer, and the electric potential falls faster with distance [15]. When the maximum of the curve of total potential is reduced, coagulation may occur. In this way, the compression of the double layer may cause the energy barrier to disappear.

3.2. Effect of oil and surfactant concentrations on destabilizing dose

The influence of oil and surfactant concentrations while keeping constant the other variable was analyzed with four emulsions, wherein NaCl concentration was maintained at 10^{-3} mol/l. Two concentrations (0.2 and 0.05 g/l) of SDS as emulsifier were used; oil concentrations were maintained constant at two levels: 1.33 and 5 g/l (Table 2).

Differences in the performance of chitosan, polyacrylamide and aluminum sulfate treatments were significant. Experiments with polyelectrolytes (chitosan and polyacrylamide) showed that an increase of surfactant concentration from 0.05 to 0.2 g/l increased 8 times chitosan dose and 4 times of polyacrylamide dose. An increase of initial oil concentration from 1.33 to 5 g/l, while maintaining surfactant concentration constant, doubled chitosan dose, but did not modify polyacrylamide dose.

Doses of aluminum sulfate to reach zero colloidal charge were not significantly different for the tested systems (Table 2) in spite of having different initial charge. Thus, a stoichiometric relationship between coagulant concentration and initial colloidal charge was not observed.

A linear relationship between initial colloidal charge and flocculant doses to reach zero charge was observed only for chitosan treatment [16].

3.3. Effect of pH

Emulsions containing 0.2 g/l SDS, 5 g/l sunflower oil and 10^{-3} mol/l NaCl were used to study pH effect by adding HCl or NaOH. The pH of the original emulsion (control) was 5.8.

Considering the relevance of pH on the hydrolysis products of aluminum sulfate and the colloidal charge of the system, different experiments were designed to analyze pH effects.

Table 1
Doses of chitosan, polyacrylamide and aluminum sulfate to reach zero colloidal charge for emulsions formulated with 5 g/l oil, 0.2 g/l sodium dodecyl sulfate and NaCl 10^{-3}, 10^{-2} and 10^{-1} mol/l

Destabilizer agent	NaCl concentration (mol/l)	Initial colloidal charge (mequiv/l)$\times 10^3$	Zero colloidal charge dose (mg/l)[a]
Chitosan			65±2
Polyacrylamide	10^{-3}	−1.24	120±11
Aluminum sulfate			210±15
Chitosan			48±2
Polyacrylamide	10^{-2}	−1.08	105±12
Aluminum sulfate			170±12
Chitosan			33±1
Polyacrylamide	10^{-1}	−0.76	83±6
Aluminum sulfate			120±6

[a] Value±standard deviation.

Table 2
Initial charge of emulsions with different concentrations of sunflower oil and sodium dodecyl sulfate (SDS) containing 10^{-3} mol/l NaCl and doses of destabilizers (polyacrylamide, chitosan and aluminum sulfate) necessary to reach zero colloidal charge

Oil (g/l)	SDS (g/l)	Initial charge (mequiv/l)$\times 10^3$	Doses to reach zero colloidal charge (mg/l)		
			Aluminum sulfate	Polyacrylamide	Chitosan
5	0.2	−1.24	210	120	65
1.33	0.2	−0.65	180	117	28
5	0.05	−0.45	170	28	7.5
1.33	0.05	−0.21	n.d.[a]	26	3.5

[a] n.d., Dose to reach zero colloidal charge was difficult to be detected.

When pH was not controlled, it decreased as aluminum sulfate was added. Doses of aluminum sulfate ranging between 50 and 1000 mg/l were applied, obtaining a minimum turbidity of 35NTU. Fig. 3 shows the decrease of pH when aluminum sulfate concentration increased and the dose to reverse colloidal charge (210 mg/l). Increasing aluminum sulfate doses led to a pH decrease due to aluminum hydrolysis; hydrolysis products with positively charged ions like $Al(OH)^{++}$ and $Al_8(OH)_{20}^{4+}$ can be adsorbed on negative particles reducing the charge and changing the sign of the charged particles. Destabilization is mainly due to the formation of these compounds although hydroxide precipitation has an important role as well.

In a second experiment, two aluminum sulfate coagulant concentrations were selected: 200 and 500 mg/l; after aluminum sulfate was added in both cases, pH was brought to values near 6–6.5 with NaOH, because the minimum solubility of Al^{+3} occurred at this pH and aluminum hydroxide precipitated. With regard to the selected concentrations, 200 mg/l maintained negative colloidal charge and 500 mg/l reversed the charge sign. With 200 mg/l aluminum sulfate, (at pH 6), emulsion was clarified and turbidity decreased to values as low as 15.8 NTU. When more NaOH was added and alkaline pH was reached, the emulsion became turbid again. At pH 6, turbidity did not change almost with time; at any pH different from 6 turbidity remained at higher values than that of pH 6. Similar results were observed with the addition of 500 mg/l aluminum sulfate, obtaining also minimum turbidity at pH 6.

To analyze the sequence of the reactants addition NaOH was added to reach pH 6 previous to aluminum sulfate treatment; this procedure was not as effective as the previous one in producing clarification. Results may be explained considering the following equilibrium that shifts to the right side with increasing pH:

$$Al^{+3} \rightarrow Al(OH)^{2+} \rightarrow Al(OH)_2^+ \rightarrow Al(OH)_3 \rightarrow Al(OH)_4^-$$

At low pH only, Al^{+3} exists in a significant amount; when pH shifts to alkaline values hydrolysis is produced and aluminum hydroxide precipitates, although this
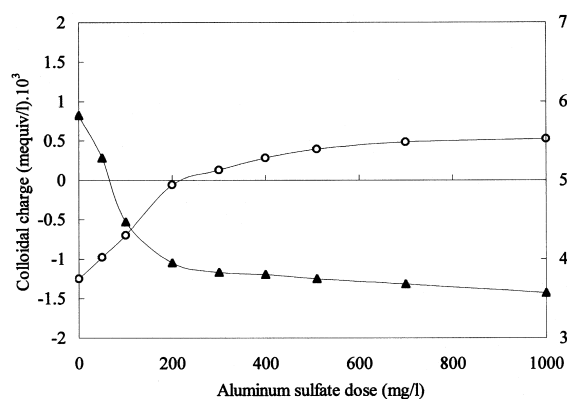

Fig. 3. (○) Colloidal charge and (▲) pH as a function of aluminum sulfate dose for an emulsion formulated with 0.2 g/l sodium dodecyl sulfate, 5 g/l oil and 10^{-3} mol/l NaCl.

occurs in a narrow range around pH 6. A pH increase led to a dissolution of the precipitate formed by $Al(OH)_4^-$ and destabilization of the colloidal system was not observed.

The effect of emulsion pH on the performance of the tested polyelectrolytes was also analyzed. The original emulsion and an acidic emulsion at pH 3.5 were treated with the cationic polyacrylamide using doses that ranged between 50 to 200 mg/l. For the acid emulsion the minimum turbidity (1.6 NTU) was attained with 150 mg/l polyacrylamide; higher doses than 180 mg/l of polyacrylamide led to restabilization of the emulsion.

In another experiment the original emulsion was brought to pH 8 with NaOH and then treated with polyacrylamide ranging between 70 and 300 mg/l (Fig. 4). Non significant differences in turbidity versus dose behavior were observed between the original emulsion and those at other pH values. In all cases, polyacrylamide addition produced clarification and restabilization of the emulsions (Fig. 4). Doses to reach minimum turbidity were shifted to higher concentrations of polyacrylamide for both acid and alkaline emulsions; however in the case of alkaline pH the range of doses was wider.

For emulsions treated with chitosan, the doses necessary to reverse colloidal charge were 67, 65, 68 and
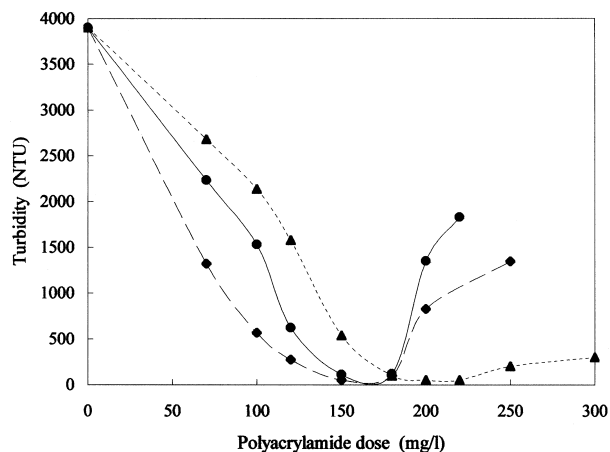
Fig. 4. Effect of pH on the curves of turbidity vs polyacrylamide dose for emulsions formulated with 5 g/l oil, 0.2 g/l sodium dodecyl sulfate and 10^{-3} mol/l NaCl: (◆) pH 3.5, (●) pH 5.8 and (▲) pH 8.

64 mg/l for pH values of 4, 5.8, 7, and 8, respectively; these results indicated that pH had no significant effect ($P < 0.05$) on the optimum chitosan dose in the tested range.

3.4. Time to achieve minimum turbidity of the system

To analyze the rate at which aluminum sulfate acts compared to that of polyelectrolytes, an emulsion containing 10^{-3} mol/l NaCl, 0.2 g/l SDS and 5 g/l oil was tested. Initial and residual turbidity were measured as a function of time, considering zero time when agitation was stopped. For aluminum sulfate, the applied doses were 200, 300 and 500 mg/l. With 200 mg/l aluminum sulfate turbidity remained almost constant after agitation was stopped; with 300 mg/l, turbidity remained constant between 30 and 120 min. Applying 500 mg/l the decrease of turbidity was most marked within the two first hours (Fig. 5).

In the emulsions treated with 100 mg/l chitosan, turbidity reached final values immediately after agitation and no significant differences were observed with time. A similar trend showed emulsions treated with 120 mg/l polyacrylamide (Fig. 5). However, an important difference between chitosan and polyacrylamide treatments was observed: in the case of chitosan treatment flocculation occurred immediately after its addition while for polyacrylamide treatment destabilization was attained during agitation. Thus, chitosan destabilization required a shorter agitation time compared to that of polyacrylamide. As can be observed in Fig. 5 the only coagulant that changed turbidity values during the 4-h test duration was aluminum sulfate.

3.5. Comparison of destabilizing mechanisms

Comparison of the action mechanisms for the tested destabilizers is not well discussed in literature. Results
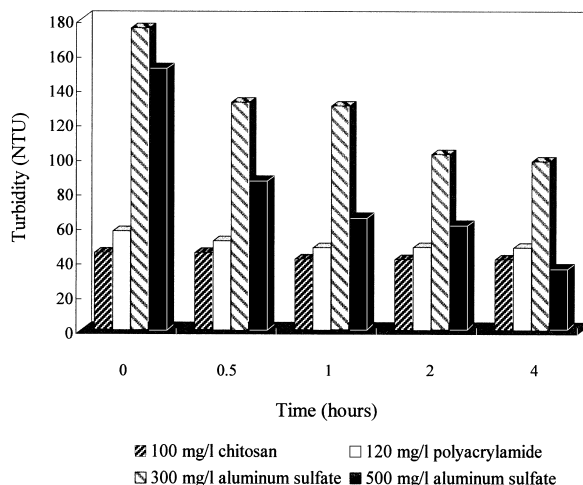

Fig. 5. Turbidity as a function of time for an emulsion formulated with 0.2 g/l sodium dodecyl sulfate, 5 g/l oil and 10^{-3} mol/l NaCl treated with different destabilizers.

obtained in the present work allowed to analyze the physico-chemical models that interpret the experimental findings.

In aluminum sulfate treatments the following results were obtained: (1) a non-stochometric relationship between coagulant and initial colloidal charge; (2) pH showed a marked effect on aluminum sulfate performance; the optimum pH to destabilize the emulsion systems was approximately 6; (3) the time necessary to produce the clarification of the system was shorter for higher coagulant concentrations; this result may be attributed to the formation of soluble compounds and the later aluminum hydroxide precipitation; and (4) colloidal charge was reversed but restabilization of the emulsion once minimum turbidity was achieved did not occur or was blurred by hydroxide precipitation.

Destabilization by aluminum salts cannot be completely described neither by the double layer model nor by the bridging model [14]. The double layer model predicts that the concentration of coagulant necessary to destabilize a colloid is virtually independent of initial colloidal charge and colloid concentration; reversion of colloidal charge and system restabilization cannot occur; electrostatic interactions are predominant and chemical interactions and adsorption are absent; zeta potential for optimum aggregation is near zero.

In contrast, the bridging model predicts that the relationship between the dose of coagulant necessary to destabilize a colloidal system is stoichiometric and restabilization is considered possible; [14] chemical interactions and adsorption are predominant mechanisms.

Analyzing these concepts, the proposed mechanism for aluminum sulfate treatment is based on a destabilization model by hydrolyzed metal ions, in which electrostatic attraction, chemical forces and adsorption are

all important; these findings are in agreement with Stumm and O'Melia [14] reports.

In polyelectrolyte treatment (chitosan or polyacrylamide) it was found in the present work: (1) reversion of the colloidal charge; (2) restabilization of the emulsion when an excess of the destabilizer was added; and (3) coincidence between the doses producing zero colloidal charge and minimum turbidity.

A linear relationship between initial charge and flocculant dose necessary to reverse the sign of the colloidal charge was only observed for chitosan treatment. This relationship was not found for aluminum sulfate nor for polyacrylamide. Non-significant effect of pH was observed in chitosan treatment; when polyacrylamide was applied, pH of the emulsion only produced a shift of the destabilization dose range.

The main difference between both polyelectrolyte treatments was the time necessary to destabilize the emulsions after flocculant addition; chitosan produced destabilization instantaneously but not polyacrylamide.

Results showed that charge neutralization and bridge formation were found to be important action mechanisms in polyelectrolyte treatments. Charge neutralization seems to be more relevant for chitosan, since a sharp coincidence between zero colloidal charge and minimum turbidity was found. Besides, bridge formation mechanism would explain restabilization of the emulsions when doses of polyelectrolyte were higher than those producing minimum turbidity.

4. Conclusions

The application of polyelectrolytes in doses higher than those giving the minimum turbidity, led to emulsion restabilization and to an abrupt turbidity increase. In aluminum sulfate treatments once the emulsions were destabilized and reached low turbidity values, further addition of the coagulant did not produce restabilization. A close relationship between colloidal charge and turbidity was observed in all cases, while the emulsion colloidal charge was near zero, turbidity remained at the minimum values; the emulsion restabilization was accompanied by a reversal of the colloidal charge.

The increase of NaCl concentration reduces the doses of chitosan, polyacrylamide and aluminum sulfate necessary to produce destabilization and flocculation; the thickness of the double layer and the repulsive forces decrease when ionic strength increase.

The increase of surfactant chain length (STS respect to SDS) increased, the doses necessary to produce destabilization and to reach zero charge for all the tested destabilizers. This implies that the hydrophobic part of the surfactant plays an important role in the interaction between surfactant and flocculant.

The system pH (range 4–8) showed no influence on the chitosan dose necessary to flocculate the emulsion. In the case of polyacrylamide, the range of doses to reach the minimum turbidity for alkaline emulsions was wider. However the pH showed a marked effect on aluminum sulfate performance; the optimun pH to destabilize the system was approximately 6.

Emulsion treated with the optimum chitosan doses were clarified immediately, once the focculant was added. Polyacrylamide produced a rapid turbidity decrease (but not instantaneous), when the flocculant was added. In the case of aluminum sulfate, the time needed to produce clarification was longer than for polyelectrolytes and depended on the applied doses. This longer time may be attributed to the formation of soluble compounds and the later aluminum hydroxide precipitation. With regard to the mechanisms of action, charge neutralization is probably the most relevant for chitosan treatment; in the case of polyacrylamide bridging mechanism, has also be considered. For aluminum sulfate treatment a destabilizing model by hydrolyzed metal ions, in which electrostatic attraction, chemical forces and adsorption are all relevant.

Acknowledgements

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