Optimal clarification of emulsified oily wastewater using a surfactant/chitosan biopolymer

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ABSTRACT

The presence of emulsified oils in wastewater from the petroleum and petrochemical industry causes a significant environmental concern. The effect of chitosan (CH) and sodium dodecyl sulfate (SDS) doses on the destabilization of emulsified wastewater was analyzed based on key parameters such as: residual turbidity (% RT), relative length of the clarified zone (CL), chemical oxygen demand (% COD) and zeta potential (ZP).

A response surface methodology and central composite design were applied for optimizing the influence of CH and SDS doses, on the performance of the demulsification process. A desirability test allowed to calculate the optimal doses of CH and SDS to produce: i) minimum values of %RT and ZP and ii) maximum values of CL and % COD removal.

A novel kinetic model based on first order equations for both stages: coagulation/flocculation and settling of the flocs was proposed to describe clarification using measurements of static dispersion of light and back scattering profiles (BS). The proposed model is a useful tool for predicting clarification times and to analyze the governing mechanisms of the process.

Coagulation/flocculation occurs in less than 3 h reaching very low turbidity values in the clarified zone (< 11% RT). Additionally, the BS profiles after 3 h showed that at the optimal dosage of CH and SDS 70% of the total volume was clarified with a total hydrocarbon removal of 98.61%.

This study demonstrates that CH constitutes a potent flocculating/coagulating agent in waste-water emulsified systems from petroleum industry.

1. Introduction

Oily wastes represent one of the most important challenges in petroleum and petrochemical industry. Significant part of oil is normally present in the emulsified form that is difficult to separate from the water phase [1,2]. The presence of emulsified oils in wastewater causes a significant environmental concern; besides, they have a very strong negative influence on the performance of physical operations and biological water treatments [3,4]. Therefore, destabilization of oil/water emulsions remains a main step in most technological setups of oily waste treatments.

Coagulation/flocculation (C/F) is one of the most efficient and simplest methods adopted in water treatment industries to achieve solid-liquid separation. During C/F processes, the small colloids suspended in wastewater are destabilized by the addition of coagulants. Coagulation is followed by flocculation, in which the destabilized particles (very small droplets of the emulsion) aggregate forming larger flocs that can be removed by sedimentation [5].

Various chemical agents can be applied, to enhance oil and water separation through neutralization of the surface charge of the emulsion droplets, leading to demulsification and agglomeration of oil droplets into the large flocs [2]. Flocculants are in general classified in two groups: i) inorganic coagulants, such as aluminum sulfate, poly-aluminum chloride, and polymerized ferrous sulfate and (ii) synthetic and natural organic polymeric flocculants [5]. Traditional inorganic salts of multivalent metals have been widely used as coagulants because their low cost [5]. They are often preferred for their adsorption on negatively charged colloidal particles, resulting in simultaneous surface charge

Nomenclature

% COD	Chemical oxygen demand removal
% RT	Residual turbidity
CL	Relative length of the clarified zone
d	Desirability
D	Global convenience value
$dj(Yj)$	Desirability value for each response from the experimental desing
dj	Desirability function response
k	Number of factors
k_{CF}	Kinetic coefficients coagulation/flocculation process
k_d	Number of responses to determine global convenience value
k_S	Kinetic coefficients of settling process
L	Length of the turbid zone
L_{0CF}	Initial conditions of coagulation/flocculation process
L_{0S}	Initial conditions of settling process
L_T	Total length of the sample
N	Number of experiments required
n_c	Number of replicates at the center point
N_F	Number of points in the cube portion of the experimental

	design
R^2	Determination coefficient
S	Settling process
t	Time
X_1	Independent variables (sodium dodecyl sulfate)
X_2	Independent variables (chitosan)
x_f	the value at the center point
$\hat{Y}$	Predicted response
Yj	Response of desirability function

Greek letters

α	Star points experiment desing
α_{CF}	Coagulation/floculation fraction
α_S	Settling fraction
β_i	Coefficients of the model; $i=1$ corresponds sodium dodecyl sulfate, $i=2$ corresponds chitosan
β_{ij}	Interaction between indepent variable
δ_x	Step change
λ	Wavelength
ξ_i	Uncoded factor
χ_i	Coded value of factor

reduction and formation of micro-flocs. Therefore, large doses of inorganic coagulants are usually required for efficient flocculation, producing large volumes of metal hydroxide sludge and subsequent disposal problems. However, inorganic coagulants are highly sensitive to pH and inefficient towards very small particles [6]. Moreover, an increase in metal concentration in treated water may have serious human health concerns. The use of aluminium salts was reported to have adverse impacts on human health; low levels of aluminium can lead to behavioral and morphological changes associated with Alzheimer's disease and age-related neurodegeneration [7,8].

Polymeric flocculants are generally divided into four categories, which include non-ionic, cationic, anionic, and amphoteric polymers [9]. Organic polymer flocculants have different chemical composition, molecular weight, degree of substitution of the functional groups, structure, ionic nature and charge density being highly efficient with low doses (e.g. few mg/L); they generate much smaller sludge volume without consumption of alkalinity unlike inorganic coagulants. The flocs formed during flocculation are in general larger and stronger, exhibiting excellent settling characteristics [10,11].

It is important to remark that polymeric flocculants, especially cationic polymers, can be used in direct flocculation processes, because they have dual functions of coagulation and flocculation, neutralizing the negative charges and bridging the aggregated destabilized particles [12,13].

However, synthetic organic polymer flocculants such as polyacrylamide (PAM) and its derivatives present severe problems related to the residual unreacted monomers including acrylamide and ethyleneimine, that are toxic and produce neurotoxic effects [9]. Although PAM is one of the chemicals with the largest production volume, the high toxicity associated with acrylamide is of environmental and human health concerns. It is a challenging process to design and develop non-PAM-based flocculants [9].

In contrast, the application of natural polymeric flocculants constitutes a better alternative due to their nontoxicity, and biodegradability. The tendency is to find more economical, sustainable and ecologically compatible processes, such as the application of biopolymers to avoid the generation of hazardous residues. One of the biopolymers most used as a coagulant in the treatment of wastewaters from different industrial activities is chitosan (CH), which is a linear polysaccharide and is prepared by deacetylation of the acetamide groups of chitin. Chitin is the second most abundant natural polymer, only surpassed by

cellulose, making it an important renewable resource. Chitin is extracted from the shells of crustaceans, such as crabs, shrimp etc [14]. Chitosan consists of chains of β-(1-4) D-glucosamine (deacetylated units) and N-acetyl-D-glucosamine (acetylated unit), its main difference with chitin is the presence of amino groups (-NH$_2$) which give it a character of natural cationic polyelectrolyte in acid medium with important technological applications [4,5].

Natural bioresource-based flocculants have recently emerged as promising environment-friendly alternatives [4]. Among these bioresource-based flocculants, CH one of the most abundant polysaccharides with relatively low cost, has attracted considerable attention since it can be obtained from the solid waste of the seafood processing industry.

The cationic properties of CH make it easier to flocculate the negatively charged emulsified oil droplets via electrostatic interaction. As compared with traditional flocculants, such as polyaluminum chloride or cationic polyacrylamide it was reported that CH showed better flocculation effect for treating emusilfied oily wastewaters [15]. The main flocculation mechanism of CH under acidic condition was reported to be charge neutralization. Charge patching and sweep floc were described for neutral and alkaline conditions, respectively [4].

Guibal et al., [16] and Renault et al., [17] published interesting reviews related to the application of CH as a flocculant. Renault et al., [17] reported an overview of the C/F performance of CH for various pollutant suspensions and solutions. These reviews described the relevant C/F mechanisms and the effects of CH characteristics on its performance. However, these studies did not include chemically modified chitosan flocculants. Yang et al., [5] described the use of CH and its derivatives as flocculants for the treatment of different types of wastewater. They analyzed several of the chemical modification methods commonly used to prepare chitosan-based flocculants. These methods allow convenient control and adjustment of the structures of the obtained materials to meet the different practical requirements. Additionally Zhang et al., [4] reported that grafting has been proved as a useful and convenient modification method to improve flocculant performance and demonstrated that CH-based graft copolymers exhibited more efficient flocculation performance than that of CH.

The charge density along the CH chains and, therefore, its flexibility can be tailored by changing the deacetylation degree (DD). These properties, together with the hydrophobicity of the backbone, may play an important role on the interactions of CH with amphiphilic molecules,

such as surfactants. Surfactants in oily waste water can be used to enhance the bioavailability of hydrophobic organic pollutants through: 1) emulsification of the non-aqueous phase pollutant, 2) enhancement of the apparent solubility of the pollutant by the presence of micelles, and 3) facilitated transport of the pollutant [18].

Petroleum-in-water emulsions exhibit higher stability in the presence of surfactants that contributes the oil phase to remain dispersed. Sodium dodecyl sulfate (SDS) is an anionic surfactant of the alkylsulfate family composed of a chain of twelve carbon atoms linked to a sulfate group giving the molecule amphiphilic properties [19,20] SDS has a high degree of biodegradability [21] and its role in oil/water emulsions is very important.

When SDS is added to an emulsion at a concentration below the critical micelar concentration, the surfactant surrounds the oil droplets conferring a negative charge to the emulsion. When SDS is added to an oil/water system, the surfactant surrounds the oil droplets conferring a negative charge to the emulsion occupying (or filling) the interfacial region until a significant portion of the surface layer is packed with surfactant. When the maximum coverage is reached, the surfactant will form micelles in the bulk phase; this concentration is called the critical micelle concentration [22].

The addition of CH (cationic polyelectrolyte) as destabilizing agent will neutralize the negative charges of the emulsion; however, the excess of SDS will interact with CH. Petrović et al., [23] reported that CH/SDS association is a cooperative phenomenon where surfactant binds to the polymer in the form of aggregates, usually through electrostatic or hydrophobic forces. Polyelectrolytes such CH interact with oppositely charged surfactants through electrostatic attraction that results in polymer/surfactant complex formation. Chitosan/SDS complexes are stabilized by combination of electrostatic, ion-dipol and hydrophobic interactions and can be formed even when the surfactant concentration is below its critical micelle concentration.

As it is observed, complex phenomena occur during demulsification, when a cationic polyelectrolyte is added in the presence of an anionic surfactant; then it is important to analyze the combined effect of different doses of SDS and CH in crude oil emulsions, in order to determine the optimal concentrations of these agents with the purpose of finding an optimium clarification of oily wastewater.

The knowledge of the kinetics involved during the C/F and later sedimentation of the flocs can be considered as a useful tool for designing adequate equipment and residence times, however information about this subject in literature is scarce.

The objectives of the present study were:

a) To analyze the effect of CH and SDS doses on the demulsification of emulsified waste water containing various concentrations of crude oil, based on the following measurements in the clarified phase: residual turbidity (% *RT*), relative length of the clarified zone (*CL*), chemical oxygen demand removal (% *COD*), residual concentration of total hydrocarbons and zeta potential (ZP).

b) To apply a response surface methodology (RSM) and central composite rotatable design (CCRD) for modeling and optimization the influence of CH and SDS doses (operating variables), on the performance of the demulsification process.

c) To determine the optimal doses of CH and SDS to produce in the clarified phase: i) minimum values of% *RT* and ZP and ii) maximum values of *CL* and%*COD* by using the desirability test in this multiple response problem.

d) To validate the predictive model and to develop a practical method based on the optimized results that allows the application of adequate doses of CH and SDS to demulsification and clarify crude oil/water emulsions in a wide range of concentrations.

e) To analyze the kinetics of demulsification based on photographic records and measurements based of the phenomenon of static dispersion of light.

Table 1
Main physical and chemical characteristics of the crude oil used, these were provided by the company Argentina YPF.

Density	0.8855 g/mL
Water content	0.560% (w/w)
Salt content	60.0 mg_{salt}/Kg_{oil}
Sediment content	0.038% (w/w)
Number acid	0.8220 mg_{KOH}/g_{oil}
Sulfur content	0.1890% (w/w)
Kinematic viscosity at 40 °C	30.4 mm^2/s
Pour Point	−6 °C

2. Materials and methods

2.1. Emulsified wastewater model systems

The coagulation/flocculation (C/F) studies were carried out using oil/water emulsions, formulated with (i) crude oil (petroleum) from the Argentina Patagonia, (ii) distilled water and (iii) sodium dodecyl sulfate (SDS) (Biopack, Argentina, MW = 288.37 g/mol). Main physical and chemical characteristics of the crude oil were provided by the Refinery YPF (Argentina) and are shown in Table 1.

The pH of the medium was adjusted with 0.1 N sodium hydroxide and hydrochloric acid emulsified systems were obtained with Ultra Turrax T-25 equipment (Janke & Kunkel GmbH, Staufen, Germany) at a speed of 13500 rev min^{-1} during 5 min, the amount of crude oil and SDS varied according to the type of test.

The emulsions used in C/F assay had a diameter weighted mean value by volume (D[4,3]) of crude oil droplet of 13.13 (0.07) μm (in parenthesis standard deviation). The D[4,3] was determined by microscopic observations on a microscope coupled to a DC 100 camera (Leica Microscopy Systems Ltd., Heerbrugg, Switzerland). The flocs were stained with Direct Red 23 an anionic dye in order to visualize the structure of the flocs.

Several authors analyzed the interactions between SDS and CH solutions. Barreiro-Iglesias et al., [24] studied the thermodynamics of the binding process of SDS to CH and the ionic and hydrophobic interactions. They concluded that as SDS concentration increased, CH solutions showed a typical phase separation; large aggregates were observed to be formed at different SDS concentrations. The addition of increasing amounts of SDS resulted in a decrease of the CH solution viscosity above the critical aggregation concentration; however when one third of the polymer amino groups were neutralized, a macroscopic coacervation was produced.

Therefore defining the range of SDS concentration to formulate the emulsions is important in order to avoid that an excess of SDS would interact with chitosan forming hydrogels. Related to this aspect the CMC (critical micellar concentration) of SDS was determined at different pH values using the conductimetric method [25] with a conductivimeter CD-4318SD (Lutron, Taiwan).

2.2. Demulsification test

For the demulsification tests chitosan flakes (CH) Sigma (St. Louis, MO, USA) from crab shells with a deacetylation degree of 82.9% and a molecular weight of 5.75×10^5 g/mol were used. The stock chitosan solution (CHS) of 0.5% (w/v) was prepared by solubilization of the flakes in 1.5% (v/v) acetic acid Anedra (Buenos Aires, Argentina) at 20 °C under stirring for 12 h approximately. C/F was investigated in batch tests, different volumes of CHS were added to the oil water emulsions; the mixture was stirred for 30 s in a Vortex Arcano model Hx-2000-1 (Arcano, Zhejian, China) at 1200 rev.min^{-1}.

2.3. Residual turbidity and volumetric faction of the clarified fluid

After addition of CHS emulsion was destabilized and the residual

turbidity percentage (%RT) of the clarified fluid was determined by measuring the optical densities at 500 nm (D^{500}) in a UV–vis 1240 Spectrometer (Shimadzu Corporation, Kyoto, Japan). The percentage of residual turbidity (%RT) was obtained by Eq. (1).

$$\%RT = \frac{D^{500}_{\text{clarified}}}{D^{500}_{\text{emulsion}}} \times 100 \tag{1}$$

where: $D^{500}_{\text{emulsion}}$ corresponds to the stable emulsion and $D^{500}_{\text{clarified}}$ was measured in the clarified fluid after addition of CH.

The relative length of the clarified zone (CL) was determined by taking photographs after the addition of CH. The photographs were analyzed using the software ImageJ [26] and CL was calculated according to Eq. (2), where $x_{\text{clarified}}$ is the length of the clarified zone and x_{emulsion} the length of the original emulsion before the addition of CH.

$$CL = \frac{x_{\text{clarified}}}{x_{\text{emulsion}}} \tag{2}$$

2.4. Determination of chemical oxygen demand

Chemical oxygen demand (COD) was determined using a commercial test (Hach Cat. No. 8000). The results in mg/L, COD are defined as the milligrams of O_2 consumed per liter of sample under the conditions of this procedure. The sample (2 mL) was heated with sulfuric acid and a strong oxidizing agent, potassium dichromate (digestion during 2 h at 150 °C) in a Hach COD Reactor 45600 (Loveland, Colorado, USA). Oxidizable organic compounds react, reducing the dichromate ion ($Cr_2O_7^{2-}$) to green chromic ion (Cr^{3+}). Hach DR 2800 spectrophotometer (Loveland, Colorado, USA) was used for the absorbance determination of the digested samples at 620 nm.

The COD reagent also contains silver and mercury ions: silver is a catalyst, and mercury is used to complex chloride interferences. The percentage of COD removal (%COD) was calculated according to Eq. (3).

$$\%COD = \frac{COD_{\text{emulsion}} - COD_{\text{clarified}}}{COD_{\text{emulsion}}} \times 100 \tag{3}$$

where COD_{emulsion} is the COD of the stable emulsion and $COD_{\text{clarified}}$ is the COD of the clarified zone.

2.5. ZETA Potential

Zeta potential is a key measure of the surface charge of dispersed drops in an emulsion; its value is related to the structure of electrical double layer formed around the droplets [27]. The increased thickness of the electrical double layer increases the absolute value of zeta potential, the charge repulsion, and consequently the emulsion stability. Zeta potential (ZP) was determined by electrophoretic mobility measurement using a nanoparticle analyzer SZ-100-Z (Horiba Instruments Inc., Kyoto, Japan) provided with a laser diode model JUNO 10G-HO (Showa Optronics Co., Ltd., Yokohama, Japan) operating at 532 nm. ZP was determined by measuring the direction and velocity of droplet movement in a well-defined electric field, using electrode cell (carbon, 6 mm). ZP was reported as the average of measurements made on ten determinations per sample.

2.6. Total petroleum hydrocarbon content

The total petroleum hydrocarbon (TPH) content was assayed according to the Oslo Paris Commission (OSPAR) and the Department of Energy and Climate Change (DECC) of United Kingdom reference method using infrared analysis [28]. The sample was acidified to pH < 2 by adding hydrochloric acid 6 N; hydrocarbons were extracted by 10 min vigorous shaking with 25 mL tetrachloroethylene Raudo (Buenos Aires, Argentina) as solvent in a glass separating funnel. Then the solvent was drained into a 50 mL volumetric flask; this step was repeated twice with an additional 25 mL of new solvent. Quantitative analysis was performed by Fourier transform infrared spectroscopy (FTIR); spectra were recorded in absorbance mode with 34 scans and $4\ cm^{-1}$ spectral resolutions. The FTIR spectra were registered between 4000 and $500\ cm^{-1}$ using on a Thermo Nicolet iS10 spectrometer (Thermo Scientific, MA, USA). The oil content of the sample was determined by comparison of the infrared absorbances at a wavelength of $2930\ cm^{-1}$ in the extract against a calibration graph using standards containing crude oil in the range of 10–610 mg/L concentrations.

2.7. Methylene blue active substance assay (MBAS)

Residual SDS concentration in the clarified region was quantified using a modification of the methylene blue active substance assay for anionic surfactants described by Hayashi [29]. This determination is based on the formation of an ionic pair between the anionic surfactant and the methylene blue cation forming the SDS-methylene blue complex, that is miscible in chloroform allowing its quantification spectrophotometrically. The treatment of the sample was carried out in a Hach glass tube, adding 1 mL of the sample, 250 μL 0.5% (w/v) methylene blue, 250 μL phosphate buffer solution (0.7 mM pH = 7.2) and 3 mL of chloroform; this system was mixed for 1 min using Arcane

Table 2
Response surface experimental design conditions with the corresponding codes. SDS = sodium dodecyl sulphate concentration, CH = chitosan concentration.

Crude oil concentrations in the emulsions (g/L)

Experiment	2.55		1.47		1.00		0.40		Codified variables	
	SDS and CH Concentrations (g/L)									
	SDS	CH	SDS	CH	SDS	CH	SDS	CH	X_{SDS}	X_{CH}
1	1.009	0.837	0.583	0.485	0.395	0.328	0.159	0.131	0	0
2	1.298	1.257	0.756	0.727	0.510	0.492	0.216	0.197	1	1
3	1.298	0.419	0.756	0.243	0.510	0.164	0.216	0.065	1	−1
4	0.721	0.419	0.409	0.243	0.280	0.164	0.101	0.065	−1	−1
5	0.721	1.257	0.409	0.727	0.280	0.492	0.101	0.197	−1	1
6	1.009	0.837	0.583	0.485	0.395	0.328	0.159	0.131	0	0
7	1.009	0.837	0.583	0.485	0.395	0.328	0.159	0.131	0	0
8	1.009	0.837	0.583	0.485	0.395	0.328	0.159	0.131	0	0
9	1.009	0.837	0.583	0.485	0.395	0.328	0.159	0.131	0	0
10	1.009	1.429	0.583	0.826	0.395	0.559	0.159	0.224	0	1.41
11	1.416	0.837	0.828	0.485	0.557	0.328	0.239	0.131	1.41	0
12	1.009	0.247	0.583	0.144	0.395	0.097	0.159	0.038	0	−1.41
13	0.603	0.837	0.337	0.485	0.232	0.328	0.078	0.131	−1.41	0

model Vortex Hx-2000-1 (Arcano, Zhejian, China). It was centrifuged for 3 min in a Hermle Z-216MK refrigerated microcentrifuge (Hermle Labor Technik, Wehinger, Germany) at 2000 rpm and 4 °C. The non-polar phase with a light blue color was recovered for the spectro-photometric quantification of the surfactant at 652 nm (Hach DR 2800 spectrophotometer (Loveland, Colorado, USA)), using the SDS calibra-tion curve (0.4–10 mg/L or SDS) previously obtained

2.8. Experimental design for coagulation-flocculation process and statistical analysis

Crude oil/water emulsions were formulated with different oil con-tents (0.40, 1.00, 1.47 and 2.55 g of oil/L of emulsion) and SDS con-centrations; these were demulsified by adding CH in solutions (Table 2). The SDS and CH concentrations tested were chosen based on previous published works from Bratskaya et al. [2] and Pinotti et al. [15]. Moreover, the range of doses of CH and SDS used for the CCRD were pre-tested in order to assure that the response surface contained the four optimal responses (%RT, CL, %COD and ZP). Response surface methodology (RSM) was applied to analyze and optimize the clar-ification of the emulsions. A composite central rotatable design (CCRD) [30] using two factors (CH and SDS concentrations) and four responses (%RT, CL, %COD and ZP) was used.

The general objective of the methodology is to investigate the de-pendence between the experimental conditions (factors) and the re-sponses, optimizing the process with a minimum number of experi-ments [31]. The CCRD contains a fractional factorial design with center points that is augmented with a group of 'star points' that allow esti-mation of curvature. For each formulated emulsion the number of ex-periments required (N) for the CCRD was determined by Eq. (4).

$$N = 2^k + 2^k + n_c \tag{4}$$

where k is the number of factors (2); n_c is the number of replicates at the center point (5); 2^k are the factorial and star points. A total of $N = 13$ experiments was required. The star points are in general, at some value α and $-\alpha$ on each axis. The value of α for rotatability depends on the number of points in the design; it is determined as follows:

$$\alpha = (N_F)^{\frac{1}{4}} \tag{5}$$

where N_F is the number of points in the cube portion of the design ($N_F = 2^k$; $k = 2$), thus $\alpha = (2^2)^{1/4} = 1.41$.

Table 2 shows the concentrations of oil in the formulated emulsions and those of SDS and CH in the experiments carried out with the pro-posed design. The codes of the considered factors were calculated using Eq. (6)

$$X_i = \frac{\xi_i - x_f}{\delta x} \tag{6}$$

where χ_i is the coded value of factor, ξ_i is the uncoded factor, x_f is the value at the center point and δ_x is the step change.

A second order quadratic model (Eq. (7)), was proposed for each of the dependent variables (%RT, CL, %COD and ZP, these parameters were determined 3 h after the CH addition), where $\hat{Y}$ is the predicted response, X_1 and X_2 are the independent variables (concentrations of SDS and CH respectively expressed in g/L), βi are the coefficients of the model with $i = 1$ corresponds to SDS and 2 corresponds to CH; βi values correspond to the main effects and β_{ij} to the interaction.

$$\hat{Y} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2 \tag{7}$$

β values were obtained using SYSTAT 12.0 (Systat Software, Evanston, IL, USA), with a stepwise elimination methodology to de-termine the significant terms of Eq. (7). After fitting data with the model, the goodness of fit was evaluated taking into account the dis-tribution of the residuals analysis, the Lack of fit function and de-termination coefficient (R^2).

2.9. Process optimization

A methodology of "objective function or convenience", desirability (*d*) was used to optimize multiple response processes considering the experimental design used. This methodology is based on the concept that the quality of a process has multiple characteristics, all of which remain within "desired" limits. This method determines the operating conditions that provide the "most desirable" response values [32].

The *d* function approach or "objective function or convenience" is one of the most widely used methods for the optimization of multiple response processes. The method assigns a "score" to a set of responses and chooses factor settings that maximize that score; it is based on the concept that the quality of a process has multiple characteristics, all of which remain within "desired" limits [33].

The methodology consists of determining a desirability value (*dj*) represented by the function *dj(Yj)* for each response *Yj(x)* from the CCRD. In our case the responses are %RT, CL, %COD removal and ZP being $j = 4$. The function *dj(Yj)* assigns numbers between 0 and 1; *dj(Yj)* = 0 represents a completely undesirable value of *Yj(xi)* and *dj(Yj)* = 1 represents a completely desirable or ideal response value.

A particular response *Yj* can be maximized or minimized [33], in our case the following reponses: %RT, and ZP were minimized and CL, %COD removal was maximized. For each response a different desir-ability value *dj* was obtained. The individual *dj* values are combined using the geometric mean, which gives the overall desirability or global convenience value (*D*) [33,34]. Eq. (8) is used to determine D, k_d de-noting the number of responses in our case four.

$$D = \left(\prod_{j=1}^{k_d} d_j(Y_j) \right)^{\frac{1}{k_d}} \tag{8}$$

2.10. Demulsification kinetics of the crude oil emulsion

The demulsification kinetics was analyzed using an instrument based on the phenomenon of static dispersion of light with a QuickScan vertical scanning analyzer (Beckman Coulter, Fullerton, USA); this is an instrument capable of analyzing the stability of colloidal systems and concentrated dispersions. The emulsion containing SDS and destabi-lized with CH, was placed in about 65 mm height cylindrical glass cells for measurement. The sample was scanned from the bottom to the top by a monochromatic light source (near infrared light, $\lambda = 850$ nm). Changes in the sample were registered with two synchronous detectors: a transmission (T) (at 0° from the incident light) and a backscattering (BS) detector (at 135° from the incident radiation), obtaining T and BS data every 40 μm throughout the cylindrical glass cell.

This methodology allows making several measurements at different times, obtaining BS profiles as a function of time [35]. By performing successive sweeps, it was possible to record changes in the stability of the emulsion, such as coagulation and flocculation, following the moving front of the interface between the clarified zone and the settled zone of the oily system.

3. Results and discussion

3.1. Effect of SDS aggregate and initial pH of the system

Fig. 1 shows with an adequate dose of CH the formation of oily aggregates (flocs) is produced after the demulsification process leading to a minimum of %RT in the clarified region. The addition of SDS to the emulsion improves destabilization phenomenon with lower values of turbidity in the clarified zone. This occurs by mechanisms of surface charge neutralization corresponding to the interaction of the anionic surfactant (SDS) with the cationic polyelectrolyte (CH).

When the dosage of CH is insufficient the C/F phenomenon is in-complete due to low amount of positive charges provided by the
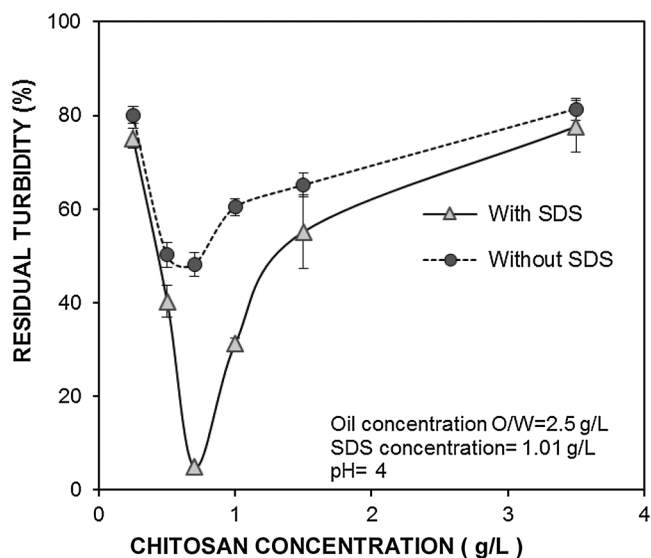
Fig. 1. Residual turbidity (% RT) of systems with and without sodium dodecyl sulfate (SDS) after the addition of chitosan in solution 0.5% (w/v). The values correspond to the mean values (n = 3) and the error bars to standard deviations.

polycationic biopolymer to neutralize anionic molecules of SDS. The performance of the clarification process deceases leaving a stable oily phase in suspension. The overdose of CH generates an increase in the% RT with respect to the optimum dose of destabilization. An excessive increase of CH can generate charge repulsion between the cationic molecules of the biopolymer causing a partial re-stabilization of the O/W particles [36], this effect is undesirable therefore it is necessary to detect the optimum dose in each case. The C/F process by CH action of the emulsified systems studied has not been affected by the initial pH of the emulsion when pH ≤ 7; these results are shown in Table 3. In the case of emulsions of sunflower oil/water, Pinotti et al., [37] observed that the initial pH of the studied systems was independent of the C/F process when they added CH; this same independence of the initial pH occurs in colloidal [38].

3.2. Optimization of coagulation-flocculation process RSM and CCRD

After checking the capacity of CH as a C/F agent, the dependence of the different responses analyzed (%RT, CL,%COD and ZP) with the most important factors that affect clarification process: concentrations of SDS and CH was analyzed.

Applying the RSM and the CCRD proposed for the different crude oil concentrations (Table 2), the coefficients (βi) of Eq. (7) were obtained, using the stepwise elimination methodology with the SYSTAT 12.0 software. These coefficients corresponding to the different responses are presented in Table 4 for each tested crude oil concentration. In all cases, the "Lack of fit" test and the determination coefficient (R^2)

showed the excellent agreement of the model with the experimental data [39]. In Fig. 2 the response surfaces obtained for a concentration of 1.47 g crude oil/L are shown. The surface responses that correspond to the dependent variables %RT and ZP show that there is an optimal minimum value in the range where the independent variables were studied (concentrations of SDS and CH). On the other hand, the behavior of the surface response shows that there are maximum values of % COD and CL in the same range of SDS and CH tested concentrations. The minimum values of % RT = 5.3 and ZP = − 0.8 and the maximum values of % COD = 73 and CL = 0.66 were reached at concentrations of SDS = 0.569 g/L and CH = 0.459 g/L. The experimental measurements were overlapped in Fig. 2a)–d) to show the satisfactory agreement of the experimental values with the predicted functions that describe the surface response of each dependent variable (% RT, ZP, CL and % COD).

3.2.1. Global desirability and statistical verification of model

Once the coefficients of Eq. (7) that describe the responses analyzed (Table 4) for the different crude oil concentrations were determined, desirability functions (dj) were defined. Table 5 shows the optimization criteria for each response. In our case the following responses (determined in the clarified zone): % RT, and ZP were minimized and the CL and % COD removal were maximized. Responses for different oil concentrations in the emulsion were obtained. Table 5 shows the predicted values of the answers according to the coefficients of Table 4 for the different concentrations of crude oil, in addition to the calculated dj.

For each response a different desirability value dj was obtained [33,34]. The individual desirabilities were combined using the geometric mean, which gives the overall desirability D (Eq. (8)), with k denoting the number of responses (in our case: four); SYSTAT 12.0 (Systat Software, Evanston, IL, USA) was used. The results of dj and D are shown in Table 5.

For the concentrations of crude oil tested, the D was > 0.9; this indicates that the optimization process was satisfactory, so applying D function the optimal amounts of SDS and CH needed to generate the C/F process were determined from the mathematical models.

The predicted optimal concentrations of SDS and CH necessary to generate the demulsification process (Table 5) were experimentally validated. An emulsion formulated with a crude oil concentration of 1.47 g/L was treated with the optimized doses of 0.569 g SDS/L, and 0.459 g CH/L obtained by the applicacion of the D function.

The results of this experiment are presented in Table 6, which shows the values predicted by the mathematical models for each response and the results obtained experimentally with their corresponding confidence intervals (CI) at 95% for a n = 3. As shown in Table 6, a very good agreement between the predicted and experimental responses were obtained which indicates that the statistical optimization process lead to satisfactory results.

The content TPH and SDS in the clarified was analyzed after 3 h; the results are shown in Table 6. After the treatment, hydrocarbon and SDS concentrations were reduced by 98.61% and 83.5% respectively.

It should be noted that Argentine regulations according to the

Table 3
Residual turbidity (% RT) obtained for O/W emulsions at different pH. The oil concentration in the experiment was 2.55 g/L and SDS was 1 g/L. Values between parentheses correspond to the standard deviation. Same letters in columns indicate nonsignificant differences by LSD Fisher Test α = 0.05, n = 3.

	Chitosan concentration (g/L)			
	0.12	0.30	0.70	1.20
% RT of clarified pH$_{initial}$ = 4	49(7) a	13.1 (0.7) a	4.9 (0.2) a	82 (1) a
% RT of clarified pH$_{initial}$ = 7	56(2) a	15.6(0.8) b	5.5 (0.3) a	89.1(0.4) b
Photographs of the O/W destabilization process (3 h) (pH = 7)				

Table 4
Coefficients determined by regressions using response surface methodology (RSM) for each analyzed response and statistical parameters (determination coefficient (R^2) and lack of fit function (p-value)). The values in parentheses correspond to standard deviation (SD). 1 = SDS; 2 = CH.

	β_0	β_1	β_2	β_{11}	β_{22}	β_{12}	R^2	Lack of fit (*p-value*)
2.55 g crude oil/L								
%RT	351 (4)	−520 (7)	−206(4)	252 (3)	106 (2)	29 (3)	0.997	0.862
CL	−2.9 (0.4)	5.5 (0.7)	2.1 (0.4)	−2.7 (0.3)	−1.16 (0.07)	−0.23 (0.08)	0.981	0.937
%COD	−274 (18)	531 (29)	198 (17)	−260 (13)	−110 (6)	−24 (1)	0.996	0.996
ZP	339 (5)	−515 (7)	−208 (4)	249 (3)	106 (2)	30 (3)	0.998	0.624
1.47 g crude oil/L								
%RT	344 (2)	−864 (7)	−373 (4)	731 (5)	356 (3)	49(5.0)	0.999	0.874
CL	−3.2 (0.5)	10 (1)	4.2 (0.8)	−8.8 (0.9)	−4.1 (0.5)	−0.80(0.09)	0.981	0.921
%COD	−350 (21)	1106 (366)	470 (23)	−934 (14)	−452 (69)	−93 (1)	0.962	0.959
ZP	293 (2)	−752 (6)	−325 (4)	635 (5)	306 (25)	49 (4)	0.997	0.956
1.00 g crude oil/L								
%RT	333 (2)	−1253(10)	−519 (6)	1550 (12)	681 (6)	184 (11)	0.999	0.998
CL	−2.6 (0.9)	13 (3)	4.9 (0.9)	−16 (5)	−7.0 (0.9)	−1.5 (0.4)	0.946	0.992
%COD	−250 (6)	1265 (333)	454 (19)	−1613 (390)	−670 (19)	−61 (2)	0.950	0.892
ZP	246 (3)	−947 (11)	−394 (6)	1162 (12)	489 (3)	187 (11)	0.950	0.914
0.40 g crude oil/L								
%RT	249 (5)	−2079 (52)	−1239(40)	6385 (146)	4183 (110)	910 (76)	0.999	0.573
CL	−2.7 (0.3)	32 (3)	17 (2)	−98 (8)	−64 (6)	−11 (9)	0.990	0.946
%COD	−263 (41)	3134(395)	1578(302)	−9683 (512)	−5581 (838)	−1161 (579)	0.978	0.747
ZP	181 (5)	−1581(48)	−931 (37)	3006 (47)	4814 (63)	908 (155)	0.999	0.690

% RT = Residual turbidity, CL = Relative length of the clarified zone, %COD = percentage of COD removal, ZP = Z Potential
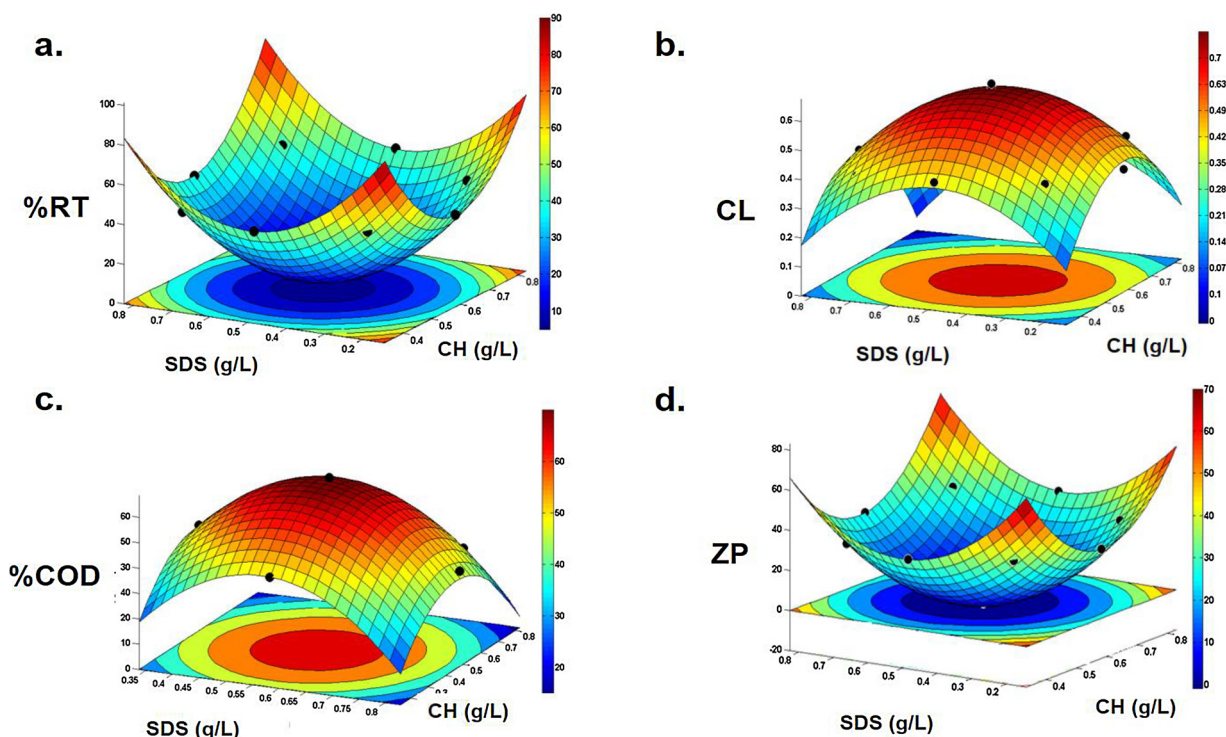
Fig. 2. Response surface plot of a) %RT, b) CL, c)%COD removal and d) ZP of the clarified zone as a function of SDS and CH concentration (g/L) considering an initial crude oil concentration in the emulsion of 1.47 g/L (COD = 2590 mg/L), (•) experimental measurements.

National Water Authority of the Province of Buenos Aires-Argentina in resolution 336/2003 the admissible limit of total hydrocarbons for the discharge of effluents in water is ≤30 mg/L; in the case of SDS the permissible limit for water discharge is 10 mg/L. It must be taken into account that the C/F is an intermediate process in the treatment of effluents before the biological stage, which is the last step of the process where the action of microorganisms decreases the organic load to a minimum.

3.2.2. Optimal doses of SDS and CH to achieve an effective clarification process

The optimal doses of CH and SDS determined from *D* function (Table 5), were plotted as a function of crude oil concentration in the emulsified wastewater, obtaining a linear relationship shown in Fig. 3.

This graph allowed calculating the amount of SDS and CH to achieve an effective clarification process. To validate the results of the proposed procedure an emulsion of 2.00 g crude oil/L was formulated and treated for clarification with the doses obtained from Fig. 3: SDS concentration of 0.773 g/L and CH concentration of 0.566 g/L. The

Table 5

Criteria used to obtain the desirability functions, predicted responses (PR), individual desirability functions (d_j), global convenience value (D) and optimal value for sodium dodecyl sulfate (SDS) and chitosan (CH) for each crude oil concentration. Values in parentheses correspond to the standard deviation.

Response variables	Optimization criteria	Crude oil concentration (g/L)							
		2.55 (COD = 4597)[a]		1.47 (COD = 2590)[a]		1.00 (COD = 1554)[a]		0.4 (COD = 727)[a]	
		PR	d_j	PR	d_j	PR	d_j	PR	d_j
%RT	Minimum	8.9 (0.3)	1.000	5.3 (0.2)	0.770	7.1 (0.2)	1.000	11.0(0.6)	1.000
CL	Maximum	0.56 (0.03)	1.000	0.66 (0.04)	0.938	0.53 (0.07)	1.000	0.70 (0.03)	1.000
%COD	Maximum	67 (1)	1.000	73 (1)	0.720	65 (7)	1.000	72 (5)	0.998
ZP	Minimum	−1.1 (0.4)	0.989	−0.8 (0.2)	1.000	0.09 (0.02)	1.000	0.96 (0.06)	0.958
Global convenience value (D)		0.937		0.984		0.921		0.986	
Optimal value	SDS (g/L)	0.986		0.569		0.385		0.147	
	CH (g/L)	0.793		0.459		0.318		0.157	

% RT = Residual turbidity CL = Relative Length of the clarified zone%COD = Chemical oxygen demand removed and ZP = Z potential

[a] COD = Chemical oxygen demand given in mg/L.

Table 6

Predicted (PR) and experimental responses (%RT = Residual turbidity, CL = length of the clarified zone, %COD = Chemical oxygen demand removed and ZP = Z Potential, n = 3) obtained for the coagulation and flocculation of the O/W emulsion with a concentration of 1.47 g/L of crude oil. The amount of sodium dodecyl sulfate (SDS) and chitosan (CH) used were obtained in the optimization process (0.569 and 0.456 g/L respectively).

		Experimental validation	
	Predicted response	Experimental response (Mean value, n = 3)	± Confidence intervals to 95%
% RT	5.34	5.22	0.37
CL	0.66	0.68	0.03
%COD	73.33	74.75	2.25
ZP	−0.755	−0.64	0.15
Characteristics of clarified[a]			
Total hydrocarbons (mg/L)		21 (7)	
SDS Content (mg/L)		94 (6)	

[a] Content of total hydrocarbons and sodium dodecyl sulfate (SDS) in the clarified after the destabilization process, values in parentheses correspond to the standard deviation for n = 3.
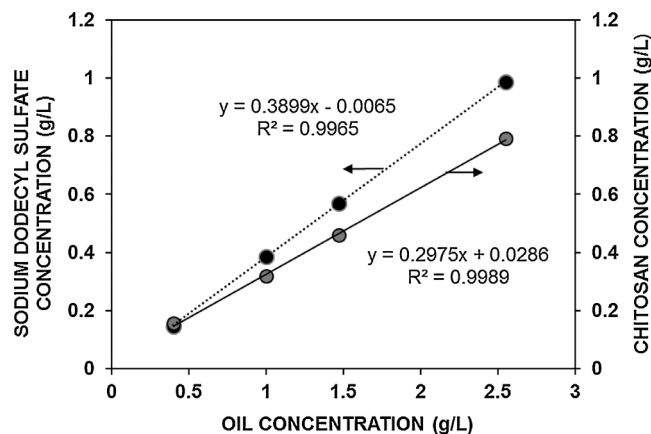
Fig. 3. Optimum values of sodium dodecyl sulfate and chitosan doses (g/L) for different concentrations of crude oil (2.55, 1.47, 1.00 and 0.40 g/L) in the emulsion.

obtained results corresponding to the experimentally determined parameters of the clarified zone are shown in Table 7 and can be

satisfactorily compared with those obtained in the statistical verification process (Table 6). It can be concluded that the clarified fluid has similar characteristics to that of the optimum clarified systems, therefore Fig. 3 provides adequate concentrations of SDS and CH for any concentration of crude oil between the tested ranges (0.40–2.55 g/L).

Moreover, the clarification potential of CH and SDS were further tested under industrial conditions in the petroleum Refinery located in the city of La Plata, Province of Buenos Aires, Argentin. The emulsified wastewater from different operating circuits were successfully destabilized using the doses obtained from the optimization methodology.

3.3. Kinetics demulsification process

Demulsification kinetics can only be measured if optimal doses of CH and SDS are added to the system. This was measured using an instrument based on the phenomenon of static dispersion of light with a QuickScan vertical scanning analyzer. The emulsion containing SDS and destabilized with CH (under optimal conditions), was placed in 65 mm height cylindrical glass cells for measurement. Fig. 4 a shows the backscattering (BS) profiles for a concentration of 1.47 g crude oil/L obtained at different times.

BS profiles as a function of time enabled to plot the length of the turbid zone (L) as a function of time (t) in order to analyze the kinetics of destabilization. L_T is the total length of the sample, L was determined by BS measurements. L/L_T is proportional to the volumetric fraction of the turbid zone.

Fig. 4b shows changes in the values of Ln (L/L_T) vs. t for two emulsified systems containing different concentrations of crude oil (1.47 and 2.00 g crude oil/L). During destabilization two stages can be observed, the first one was fast and corresponds to the C/F process. The second stage was slower and occurs during the settling of the flocs (S).

Modelling of the global destabilization kinetics was obtained by considering both consecutive stages and first order kinetic equations

Table 7

Characteristics of the clarified zone obtained for the coagulation and flocculation of the O/W emulsion with a concentration of 2.0 g/L of crude oil.

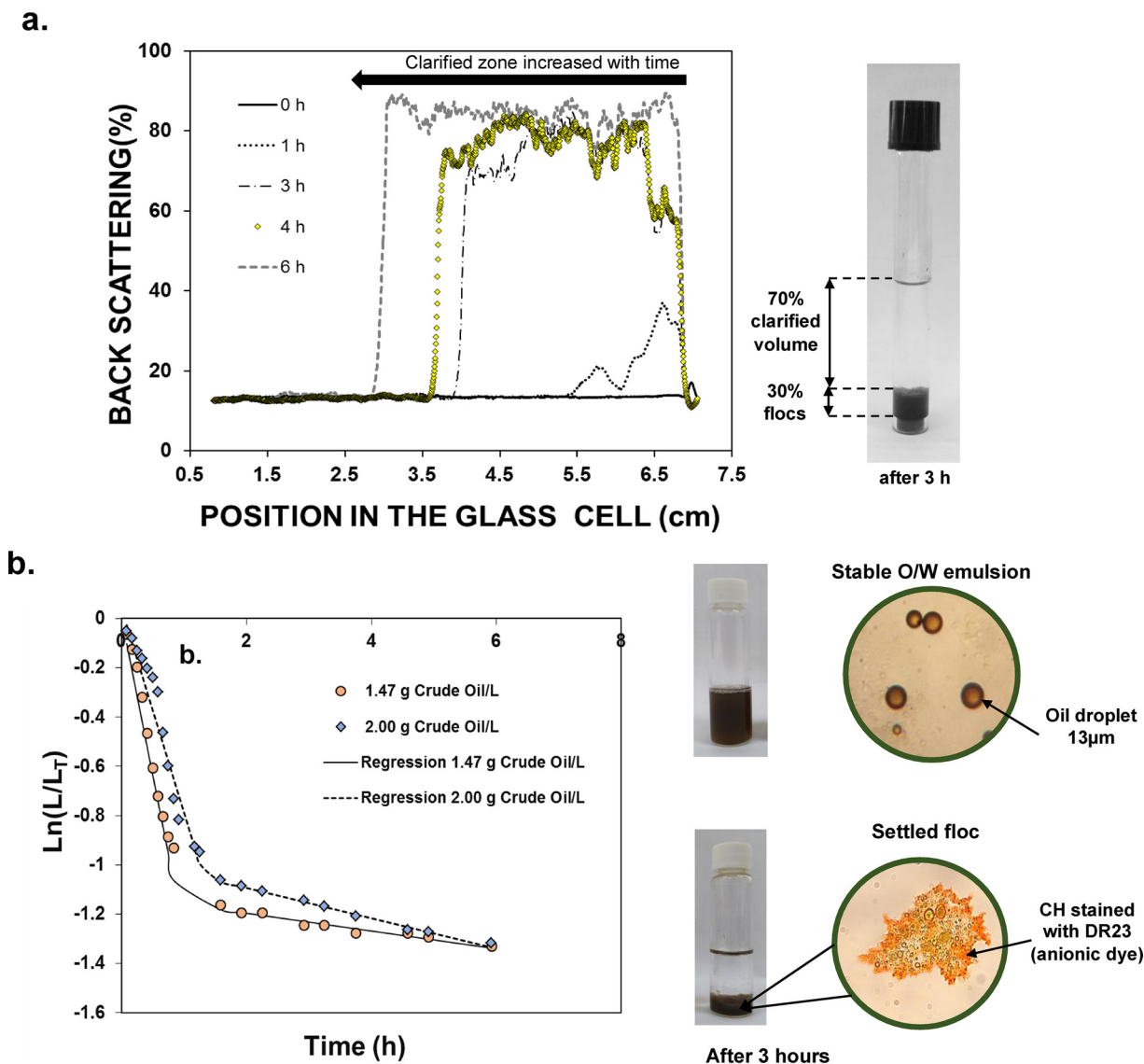| Characterisitics of the clarified zone	Experimental (Mean value, n = 3)	± Confidence Interval to 95%
% RT (Residual turbidity)	5.1	0.4
CL (Relative length of the clarified zone)	0.62	0.08
%COD (COD removal)	70.6	2.8
ZP (Zeta Potential)	−1.04	−0.02
Total hydrocarbons (mg/L)	38	6
SDS Content (mg/L)	121	9

a.

b.

Fig. 4. Results of destabilization kinetics: a). Back scattering profiles of O/W emulsion with a concentration of 1.47 g crude oil/L. Results are reported as a function of time (0–6 h) and length of the glass cell; the photograph corresponds to the sample after 3 h. b). First-order plots obtained for different concentrations of crude oil (1.47 and 2.00 g crude oil/L) in the emulsion. Symbols represent experimental values, and lines correspond to the fitting of the linear regressions.

were proposed for each one [40]. Analyzed the dynamic demulsification patterns of w/o emulsions using a pseudo-first order kinetic model, which provided a satisfactory interpretation of the experimental data under all the adopted operating conditions. At each time, the length of the turbid zone L includes the effect of both contributions Coagulation/Flocculation, (CF) and Settling (S) ($L = L_{CF} + L_S$) then:

$$\frac{dL_{CF}}{dt} = -k_{CF} L_{CF} \tag{9}$$

$$\frac{dL_S}{dt} = -k_S L_S \tag{10}$$

By integrating Eqs. (9) and (10) the following was obtained:

$$\frac{L}{L_T} = \frac{L_{oCF} \cdot e^{-k_{CF}.t} + L_{oS} \cdot e^{-k_S.t}}{L_T} \tag{11}$$

Where: t is the demulsification time (min) at a constant temperature, L_{OCF} y L_{OS} are the initial conditions at each stage and k_{CF} y k_S are the kinetic coefficients for the destabilization process (1/h).

At long times it can be considered that settling is the dominant mechanism therefore in Eq. (11), the factor $e^{-k_{CF}.t}$ tends to zero and the following is obtained:

$$\frac{L}{L_T} = \frac{L_{0S}}{L_T} \cdot e^{-k_S.t} \tag{12}$$

where:

$$\frac{L_{0S}}{L_T} = \alpha_S \tag{13}$$

On the other hand, at short times ($t \to 0$) the settled contribution was considered negligible, then $e^{-ks.t}$ tends to one obtaining:

$$\frac{L}{L_T} = \frac{L_{0CF} \cdot e^{-k_{CF}.t} + L_{0S}}{L_T} = \alpha_{CF} \cdot e^{-k_{CF}.t} + \alpha_S \tag{14}$$

where:

$$\alpha_{CF} = \frac{L_{0CF}}{L_T} = 1 - \alpha_S \tag{15}$$

The kinetic constans calculated for the different processes k_{CF} (coagulation/flocculation) and k_s (sedimentation)for two concentration of cride crude oil of: (i) 1.4 g/L: k_{CF} (h^{-1}) = 1.28 (0.06), α_{CF} = 0.68 (0.02), R^2 = 0.985; and (ii) 2.0 g/L: k_{CF} (h^{-1}) = 0.83 (0.07),

$\alpha_{CF} = 0.64$ (0.03), $R^2 = 0.943$. For the second stage (setting process): (i) 1.4 g/L: $k_S x10^2 (\text{h}^{-1}) = 3.61$ (0.32), $\alpha_S = 0.325$ (0.004), $R^2 = 0.941$; and (ii) 2.0 g/L: $k_S x10^2 (\text{h}^{-1}) = 0.62$ (0.02), $\alpha_S = 0.379$ (0.003), $R^2 = 0.993$.

In Fig. 4b the plotted lines correspond to the first order models proposed for each stage, showing a satisfactory agreement with the experimental data. Coagulation/flocculation occurs in less than 3 h reaching very low turbidity values in the clarified zone ($< 11\%$ RT). Additionally, the BS profiles after 3 h (Fig. 4a) showed that at the optimal dosage of CH and SDS the clarified volume fraction was high, reaching a value of 70%. The proposed first order consecutive kinetic models can be considered as a useful tool for predicting clarification times and to analyze the governing mechanisms of the desemulsification process.

4. Conclusions

The performance of CH was verified as effective destabilizing agent of petroleum emulsified systems. By using Central Composite Rotatable Design and Response Surface Methodology, optimal doses of CH and SDS in order to generate destabilization and to achieve phase separation, were determined as a function of the oil content in the emulsion.

Different techniques were used to analyze the performance of the destabilization process. By applying the desirability test in the multiple response problem, the optimal doses of CH and SDS were obtained. The objective functions were to reach minimum values of residual turbidity and Zeta potential and maximum values of relative length of the clarified zone and COD removal.

For the highest oil concentration (2.55 g/L) emulsified in water the desirability function resulted in %$RT = 8.9$, $ZP = -1.1$, $CL = 0.56$ and %$COD = 67$ applying the optimal dosages of SDS and chitosan concentration of 0.986 g/L and 0.793 g/L, respectively. These results were validated against experimental measurements and an excellent agreement with predicted values using surface response methodology was evidenced.

Backscattering profiles were used to determine the destabilization kinetics. Emulsion destabilization was represented by two stages: the first was fast and corresponded to the C/F process. The second stage was slower and occurred during the settling of the flocs. Destabilization kinetics was mathematically modeled and kinetic coefficients were obtained. Coagulation/flocculation occurs in less than 3 h reaching very low turbidity values in the clarified zone ($< 11\%RT$). Additionally, the BS profiles after 3 h showed that at the optimal dosage of CH and SDS 70% of the total volume was clarified with a total hydrocarbon removal of 98.61%.

This study demonstrates that chitosan (cationic polyelectrolyte) constitutes a potent flocculating/coagulating agent in waste-water emulsified systems from petroleum industry. The desestabilization capabilities of both CH and SDS were further corroborated with emulsified wastewater from a local Petroleum Refinery.

Acknowledgments

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