Water Resources and Industry 6 (2014) 51–63

Contents lists available at ScienceDirect

Water Resources and Industry

journal homepage: www.elsevier.com/locate/wri

Primary treatment optimization of a fish canning wastewater from a Portuguese plant

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ARTICLE INFO

Article history:
Received 6 December 2013
Received in revised form
25 June 2014
Accepted 20 July 2014

Keywords:
Coagulation–flocculation
Fish canning industry
Flotation
Wastewater treatment
Optimization

ABSTRACT

A sequence with three stages was optimized as a primary treatment for wastewaters from a fish canning industry of northern Portugal. Sedimentation tests were assessed at different times. The removal of a high fraction (75%) of oil and grease (O&G) and of some (48%) total suspended solids (TSS) occurred after a settling time of 1.5 h. Coagulant dosage and pH value were optimized in the coagulation/flocculation treatment using several organic and inorganic coagulants. Best removal efficiencies (99.2% O&G, 85.8% TSS and 25.2% dissolved organic carbon (DOC)) were reached using 400 mg/L of $FeCl_3$ at raw pH wastewater. DAF was also tested, optimizing chamber pressure and recycle ratio. Removals of 94% for O&G and 43% for TSS were achieved. The coupling of the latter two processes was also investigated, but no improvement of the previous results was observed. The best approach proved to be a decantation process followed by coagulation/flocculation treatment.

1. Introduction

Portugal is the largest fish consumer per capita in the European Union (EU) and third worldwide. Fish consumption in Portugal (55.6 kg/per capita/year) is more than twice the average consumption in

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http://dx.doi.org/10.1016/j.wri.2014.07.002
2212-3717/

the EU-2 [1]. The increase in consumption is mainly due to the consumer's perception that fish is a healthy alternative to other protein sources [2]. To meet this demand, the total fish processing has also increased. For example, in 2010, according to data from the National Statistics Institute, 42,000 tons of prepared and canned fish were processed in Portugal.

Similar to most processing industries, fish processing produces large volumes of wastewater, which contains especially organic contaminants, salts and oils dispersed therein [3]. The fish canning factories use a high variety of raw materials and depending on the particular operation, the degree of contamination may be small (e.g. washing operations), mild (e.g. fish filleting) or heavy (blood water or brine waters) [4]. Additionally, most fish canning industries located at northern Portugal only have pre-treatment of their wastewaters before discharge. All these factors together make difficult, for this type of industries, to meet the emission limit values (ELVs) for industrial wastewaters (Decree-Law no. 236/98). Due to this reason and to the implementation of strict discharge limits, it is necessary to study the application of a sustainable treatment sequence to this type of wastewaters that allows obtaining water with quality requirements for its discharge or reuse in the industrial process.

Primary wastewater treatment involves the removal of suspended solids by physical or physicochemical processes. Natural sedimentation may be assisted by the addition of coagulants and/or flocculants or carried out by centrifugation. This step also includes neutralization, stripping and removal of oil and grease by flotation.

Different processes have been described in the literature for the treatment of wastewaters with high oil and grease content, but the most commonly used are: chemical destabilization [5], membrane processes [6] and electrochemical methods [7]. The process of flotation for treating oily wastewaters was also already examined [8].

The principle of chemical destabilization of stable oil emulsions consists on canceling the energy barrier that exists between the oil droplets. This is attained by the addition of chemical compounds that neutralize the electric charge responsible by the repulsion of the droplets. The destabilized droplets are then agglomerated by coalescence or flocculation and, after that, separated by decantation, dissolved air flotation (DAF), centrifugation or filtration. The three neutralizing agents commonly used are metal salt [9], acids [10] and synthetic polyelectrolytes [11,12]. The best choice for a particular application depends on the system.

However, despite these techniques generally lead to interesting results, sometimes the characteristics of the treated effluent do not comply with the legal standards for discharge. To overcome these difficulties, dissolved air flotation (DAF) is sometimes a good solution. With DAF low density particles in suspension are brought to the surface of the liquid and removed, obtaining a clarified liquid. The suspended particles are carried to the surface by several microbubbles formed by the release of recycled water with dissolved air at high pressure into a flotation cell, at atmospheric pressure, that contains the wastewater to be treated [13]. The application of flotation to oil/water emulsions treatment was examined by Moosai and Dawe [14] and Qi et al. [15].

This work aims to optimize the primary treatment of a fish canning industry wastewater by sedimentation, coagulation–flocculation and flotation treatment processes. The treatment efficiencies were assessed in terms of total suspended solids (TSS), dissolved organic carbon (DOC) and oil and grease (O&G) removals.

2. Materials and methods

2.1. Chemicals

Two organic coagulants were provided by Rivaz Química, S.A.: RIPOL 070, a diester sulfosuccinate in propane – 1,2 diol solution, with 50–100% of sodium dioctil sulfosuccinate and 10–25% of 1,2-propanediol and RIFLOC 1815, a polyamine aqueous solution, with 25–50% of 1,2-ethanediamine polymer with (chloromethyl) oxirane and N-methylmethanamine and 18% approx. of aluminum polychloride. Solutions of five inorganic coagulants were supplied by Quimitécnica S.A. and were used without further purification: aluminum sulfate ($Al_2(SO_4)_3 \cdot 16H_2O$, 17% Al_2O_3, density = 2.7 g cm^{-3}), ferric sulfate ($Fe_2(SO_4)_3$, 44 ± 1%, density = 1.56 g cm^{-3}), ferric chloride ($FeCl_3$, 40%, density = 1.44 g cm^{-3}), calcium chloride ($CaCl_2$, 77%, density = 2.15 g cm^{-3}), polyaluminium chloride (PAX-18, 17% Al_2O_3, density = 1.36 g cm^{-3}).

2.2. Analysis of wastewater characteristics

The wastewater was obtained from a fish canning company located at northern Portugal that works mainly with sardines and mackerel and uses about 20% of public water supply fundamentally to the production process and 80% of well water for washing and cleaning. Fig. 1 presents the industry production process flowchart, where it is shown the water use in the various steps of the process, the main sources of wastewaters generated and the most important contaminants. Samples were collected at the outlet of the process, after sieving and sedimentation pre-treatments that they are subjected to.

Standard methods for the examination of water and wastewater [16] were adopted for the measurement of total suspended solids (TSS), volatile suspended solids (VSS), dissolved organic carbon (DOC), chemical oxygen demand (COD), biochemical oxygen demand (BOD), oil and grease

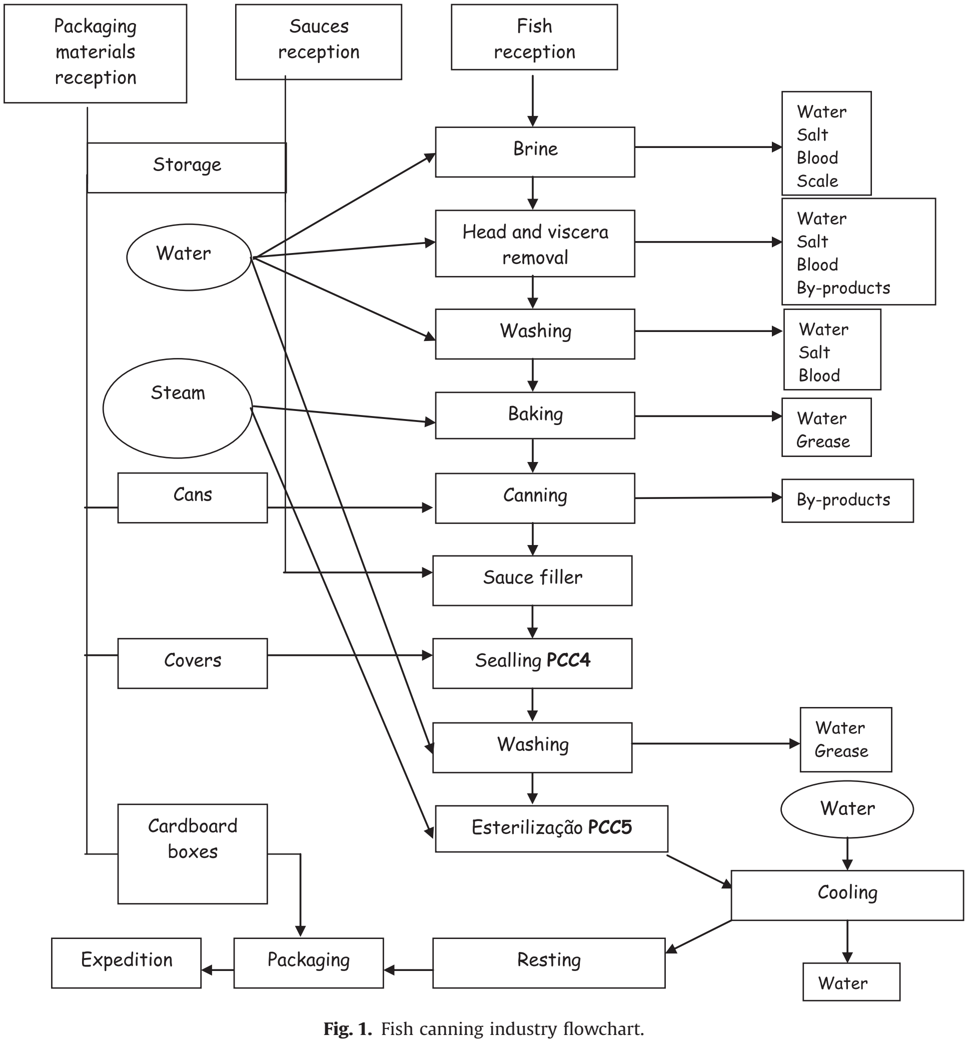

Fig. 1. Fish canning industry flowchart.

(O&G), total phosphorus (P_{total}), total soluble nitrogen ($N_{total\ soluble}$) and ammoniacal nitrogen ($N_{ammoniacal}$). For DOC measurements, prefiltered samples were injected in a Shimadzu 5000A Total Organic Carbon (TOC) analyzer. The values reported represent the average of at least two measurements; in most cases each sample was injected three times, validation being performed by the apparatus only if the coefficient of variation (CV) was smaller than 2%.

The pH was measured using a selective electrode (Hanna Instruments HI 1230) and a pH meter (Hanna instruments HI 8424) and the conductivity at 20 °C was determined using a conductivity probe (WTW TetraCon 325) and a conductivity meter (WTW LF538).

Anions were measured by ion chromatography (Dionex ICS-2100) using a Dionex Ionpac (column AS 11-HC $4 \times 250\ mm^2$; suppressor ASRS 300 4 mm). Cations were analyzed also by ion chromatography (Dionex DX-120), using a Dionex Ionpac (column CS12A 4×250 mm; suppressor: CSRS 300 4 mm). Isocratic elution was done with 30 mM NaOH/20 mM methanesulfonic acid at a flow rate of 1.5/1.0 mL/min for anions/cations analysis, respectively.

2.3. Sedimentation tests

First, to complement the screening pre-treatment at the plant, a natural sedimentation test was made, where the effluent was left in quiescence in graduated cylinders for different time periods: 0.5, 1.0, 1.5 and 2.0 h. The graduated cylinders are provided with a sampling port, 10 cm above the bottom, which allows taking samples directly from the middle layer. These samples were then analyzed in terms of TSS, DOC and O&G parameters and subsequently used in jar tests. Assays were performed in duplicate.

2.4. Coagulation/flocculation tests

A standard jar test apparatus (Jar tester JLT6, VELP Scientifica) was employed for the coagulation–flocculation tests. Five different inorganic salts ($Al_2(SO_4)_3 \cdot 16H_2O$, $Fe_2(SO_4)_3$, $FeCl_3$, $CaCl_2$ and PAX-18) were tested as coagulants. In order to evaluate the effect of the coagulant dose, several dosages (100–400 mg/L) were studied at raw wastewater pH. In a second step, the pH influence was assessed in the range of 5.0–9.0 for all the inorganic coagulants and also for two organic coagulants (RIPOL 070 and RIFLOC 1815), adopting the optimal concentrations already found in a previous work [17]. For the different tests, each jar was filled with 300 mL of sample from the sedimentation step and the coagulant dose was then added and/or the pH adjusted with 1 N H_2SO_4 or 1 N NaOH. The experimental procedure consisted of a rapid mixing at 150 rpm ($G=435\ s^{-1}$) for 3 min and, after that, in order to form flocs, the wastewater was moderately stirred at 20 rpm ($G=39\ s^{-1}$) for 15 min. Finally, a sedimentation stage allowed the flocs formed to settle. The supernatants obtained were then characterized in terms of TSS, COD and O&G.

2.5. Flotation treatment

The flotation unit consisted of a pressure retention chamber connected to an air compressor and a flotation cell of 1 L (Fig. 2). First, the flotation cell was filled with 500 mL of decanted wastewater. Then, the pressure chamber was filled to three-fourth of its volume with tap water and the water inlet valve was closed. Then, compressed air was injected to the chamber and pressurized in the range of 3.5–6.0 kg/cm^2. To dissolve the air in the water, the pressure chamber was slightly stirred for 10 min. After that, 500 mL of this air saturated water was transferred to the bottom of the flotation cell, occurring the formation of air microbubbles. At that point, the wastewater was allowed to rest for 20 min so that oil droplets reach the liquid surface attached to the microbubbles. When the flotation was completed, 500 mL of treated wastewater was taken through the sampling port, 10 cm above the bottom of the flotation cell. This procedure was repeated two more times, transferring the clarified wastewater to the pressure chamber and placing new sample of wastewater into the flotation cell. Finally, both initial and treated wastewaters were analyzed in terms of TSS, DOC and O&G for evaluating the efficiency of their removal. In addition to study the influence of pressure variation, the

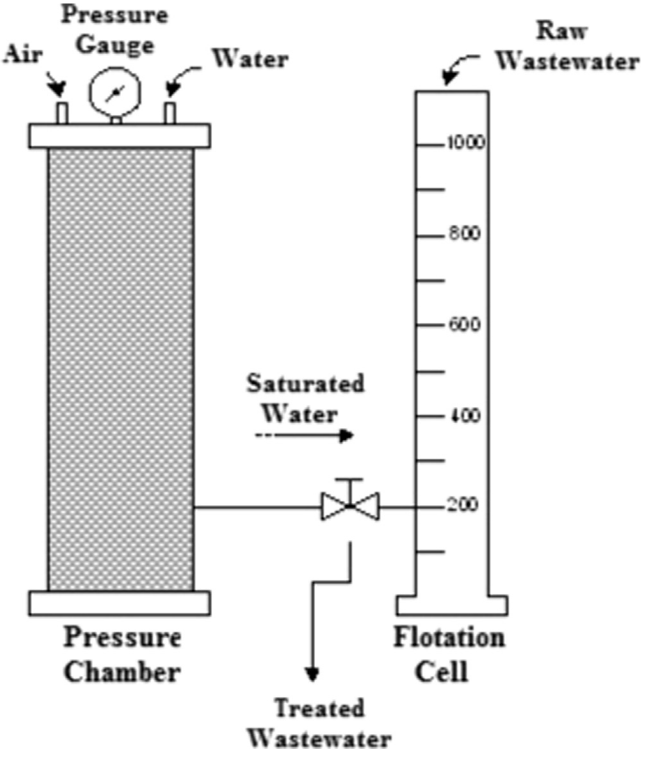

Fig. 2. Schematic representation of the dissolved air flotation unit.

recirculation ratio between the clarified effluent and the raw wastewater was also varied between 0.67 and 1.5, at the optimum pressure determined.

The performance of the flotation system depends on the air/solids (A/S) ratio defined in Eq. (1) which affects particle–bubble collision, particle separation and removal [18]

$$\frac{A}{S} = \frac{\rho_{air} S_a (fP-1)V}{RX_a} \tag{1}$$

where S_a is the air solubility in water (0.93 mL/L at 20 °C), ρ_{air} is the air mass density (1.2 g/L at 20 °C and 1 atm), f is the fraction of air saturation at pressure P (0.8 for dissolved air flotation with recirculation), P is the recycle system absolute pressure (gauge pressure, atm+1), X_a is the O&G content (mg/L), R is the pressurized water volume (L) and V is the effluent volume to be treated (L).

3. Results and discussion

3.1. Analysis of wastewaters from fish canning industries

The fish canning industries wastewaters are known to have a large variability depending on the type of fish that they are processing, on the additives that they use, on the contribution of the different industrial effluents that are being generated into the factory, etc. So, a wastewater from a fish canning plant of northern Portugal was characterized through the collection and analysis of multiple samples over a certain period of time, in order to get relevant information about its variability. Table 1 shows the seasonal variability of the wastewaters under study, after being subjected to some kind of pre-treatment (sieving, filtration, decantation,…), through maximum and minimum values of several characteristic parameters. It is possible to confirm not only the qualitative variability of this type of effluents, but also the characteristic high organic matter, oil and grease and salts contents.

3.2. Sedimentation tests

The results obtained during the sedimentation experiments showed that the formation of three different zones occurred: a floating solids layer, the clarified liquid (80% of total volume) and a bottom layer of settleable solids. The clarified liquid was then characterized in terms of TSS, DOC and O&G for each sedimentation time, giving the removal efficiencies presented in Fig. 3. It is possible to conclude that the best removals are reached after a period of sedimentation of 1.5 h, showing that there is no need to let the effluent decant for a longer time. After a sedimentation time of 1.5 h, removals of 48% of TSS and 75% of O&G were attained, in relation to the raw wastewater. In terms of colloidal and soluble organic matter removal, this treatment is not very effective, yielding a DOC removal of only 4% after 1.5 h and 6% after 2.0 h of sedimentation. This was already expected, since this is just a physical treatment that does not promote destabilization or degradation of organic matter.

Similar TSS removal efficiencies (49%) from fish canning industries effluents of Rio de Janeiro state were achieved by Aguiar and Sant'Anna [19] with a simple sedimentation of 30 min. However they attained a lower O&G removal efficiency (67%). It is important to remark that the high variability of effluent composition is responsible for a significant dispersion of pollutants removal efficiency.

3.3. Evaluation of coagulation/flocculation treatment

The clarified liquid, after 1.5 h of sedimentation, was then submitted to the coagulation/flocculation treatment, in a jar tester that allows the study of 6 different conditions at each time and thereby the optimization of coagulant type, coagulant dosage and pH value. O&G, DOC and TSS

Table 1
Seasonal variation of fish canning wastewater characteristics.

Parameter		Min	Max
pH		6.13 ± 0.01	7.14 ± 0.01
Conductivity ($mS\ cm^{-1}$)		4.73 ± 0.01	24.8 ± 0.01
TSS ($mg\ L^{-1}$)		324 ± 40	3150 ± 354
VSS ($mg\ L^{-1}$)		315 ± 44	2680 ± 735
DOC ($mg\ C\ L^{-1}$)		90 ± 19	2342 ± 47
COD ($mg\ O_2\ L^{-1}$)		1147 ± 128	8313 ± 170
BOD_5 ($mg\ O_2\ L^{-1}$)		463 ± 40	4569 ± 57
P_{total} ($mg\ P\ L^{-1}$)		13 ± 5	47 ± 5
$N_{total\ soluble}$ ($mg\ N\ L^{-1}$)		21 ± 1	471 ± 9
$N_{ammoniacal}$ ($mg\ NH_3\ L^{-1}$)		3.2 ± 0.1	1059 ± 149
Oil and grease ($mg\ L^{-1}$)		156 ± 74	2808 ± 263
Anions	F^- ($mg\ L^{-1}$)	7 ± 1	60 ± 12
	Cl^- ($mg\ L^{-1}$)	174 ± 12	5047 ± 50
	NO^{2-} ($mg\ L^{-1}$)	3.0 ± 0.5	355 ± 17
	SO_4^{2-} ($mg\ L^{-1}$)	< DL[a]	91 ± 25
	Br^- ($mg\ L^{-1}$)	< DL	214 ± 6
	NO^{3-} ($mg\ L^{-1}$)	< DL	< DL
	PO_4^{3-} ($mg\ L^{-1}$)	< DL	9 ± 1
Cations	Li^+ ($mg\ L^{-1}$)	0	1.0 ± 0.1
	Na^+ ($mg\ L^{-1}$)	86 ± 19	2120 ± 50
	NH_4^+ ($mg\ L^{-1}$)	24 ± 14	217 ± 16
	K^+ ($mg\ L^{-1}$)	5 ± 1	159 ± 23
	Mg^{2+} ($mg\ L^{-1}$)	7 ± 3	40 ± 4
	Ca^{2+} ($mg\ L^{-1}$)	60 ± 22	221 ± 39

[a] DL: detection limit.

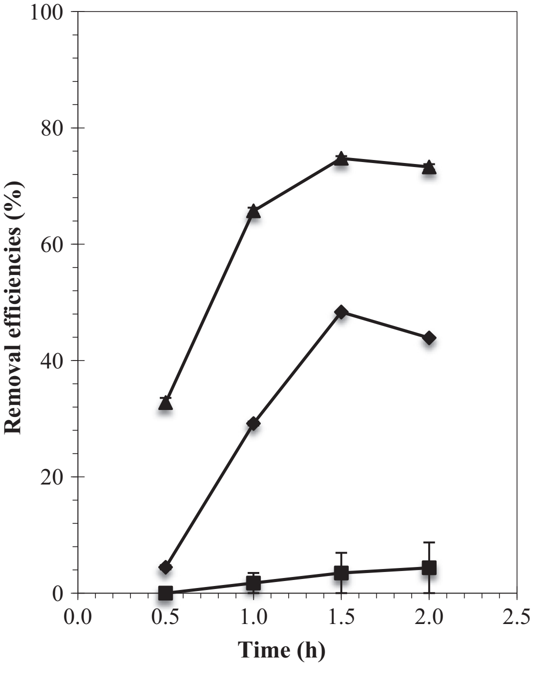

Fig. 3. DOC (■), TSS (◆) and O&G (▲) removal efficiencies of a fish canning wastewater containing 67 $mg_{O\&G}$/L, 360 mg_{TSS}/L and 694 mg_{DOC}/L, for different sedimentation times.

removals were evaluated using 2 organic coagulants (RIPOL 070 and RIFLOC 1815) and 5 inorganic salts ($Al_2(SO_4)_3 \cdot 16H_2O$, $Fe_2(SO_4)_3$, $FeCl_3$, $CaCl_2$ and PAX-18) as coagulants aids.

The coagulant dosage necessary for wastewater treatment by coagulation/flocculation depends on the wastewaters characteristics [20]. Then, coagulant dosages were primarily optimized at raw wastewater pH, to attain the maximum removals for each parameter in study. Regarding organic coagulants, this study was already reported in a previous work [17], where maximum TSS and O&G removals (79% and 99.3%, respectively) were achieved with 150 mg/L of RIFLOC 1815. However, both organic coagulants studied do not achieve good DOC removals in the dosages studied, which may be due to the high DOC contents of these chemicals. Since the best removals were observed using RIFLOC 1815, a compound that contains 18% of an inorganic salt (aluminum polychloride), this may be the reason why so good results were obtained. Thus, in order to eventually confirm this idea, additional tests using 5 inorganic salts as coagulants were performed, with concentration ranging between 100 and 400 mg/L. The results as shown in Table 2 let us to conclude that the optimal dosages corresponding to the best removal of O&G, DOC and TSS were: 400 mg/L for $Al_2(SO_4)_3 \cdot 16H_2O$, 400 mg/L for $Fe_2(SO_4)_3$, 400 mg/L for $FeCl_3$, 100 mg/L for $CaCl_2$ and 200 mg/L for PAX-18. However, in general, the salts that led to the best results were $Fe_2(SO_4)_3$, $FeCl_3$ and PAX-18. Concerning DOC and O&G, the best removals (34% and 99.5%, respectively) were obtained with 400 mg/L of $Fe_2(SO_4)_3$. Nevertheless, the best TSS removal (86%) was obtained with 400 mg/L of $FeCl_3$. Although very good removals were attained with 400 mg/L of $Fe_2(SO_4)_3$, it was verified that this coagulant contributes to the increase of suspended solids in solution, occurring the formation of iron sludge and, at the same time, the appearance of an orange color characteristic of the iron salt used, that makes difficult to determine the exact TSS removal at higher coagulant dosages. It has to be noted, that the lower removals of the three analyzed parameters were observed when $CaCl_2$ was used as coagulant.

Other authors' results show that the optimal coagulant and the respective optimal dosage depend on the properties of the wastewater to be treated. The results from this study are compared with other

Table 2
O&G, TSS and DOC removal efficiencies of a fish canning wastewater containing 759 $mg_{O\&G}$/L, 396 mg_{TSS}/L and 427 mg_{DOC}/L at different dosages of several inorganic coagulants.

Coagulant	O&G removal (%) Coagulant dosage (mg/L)			TSS removal (%) Coagulant dosage (mg/L)			DOC removal (%) Coagulant dosage (mg/L)		
	100	200	400	100	200	400	100	200	400
$Al_2(SO_4)_3 \cdot 16H_2O$	98.8 ± 0.5	99.4 ± 0.5	99.0 ± 0.5	66.5 ± 1.5	66.5 ± 0.1	76.4 ± 0.1	20.7 ± 0.1	15.2 ± 0.1	26.9 ± 0.1
$Fe_2(SO_4)_3$	99.4 ± 0.5	99.5 ± 0.5	99.5 ± 0.5	56.7 ± 1.7	0.0	0.0	29.8 ± 0.1	32.1 ± 0.0	33.7 ± 0.0
$FeCl_3$	98.4 ± 0.5	99.2 ± 0.8	99.2 ± 0.5	62.6 ± 0.1	72.4 ± 0.1	85.8 ± 0.1	19.4 ± 0.1	19.3 ± 0.1	25.2 ± 0.1
$CaCl_2$	97.0 ± 0.5	95.6 ± 0.5	94.7 ± 0.5	52.8 ± 0.2	31.1 ± 0.2	46.5 ± 0.2	16.4 ± 0.1	24.2 ± 0.1	26.4 ± 0.1
PAX-18	99.1 ± 0.5	99.5 ± 0.5	98.9 ± 0.5	76.4 ± 1.0	80.3 ± 0.1	68.5 ± 0.1	22.9 ± 0.1	26.6 ± 0.1	33.4 ± 0.0

Table 3
Comparison of O&G and TSS removal efficiencies obtained in this study with other results from literature.

Wastewater type	Coagulant type	Dosage	Removal efficiency	References
Fish canning industry wastewater	$Al_2(SO_4)_3 \cdot 16H_2O$	75–300 mg/L	86% O&G; 70% TSS	[19]
Fish canning industry wastewater	$FeCl_3$ + CaO	0.4 g/L + 0.2 g/L	73–89% O&G; 94–95% TSS	[22]
Vegetable oil refining industry wastewater	$Al_2(SO_4)_3 \cdot 16H_2O$/ $FeCl_3 \cdot 6H_2O$	250 mg/L	83%/73% O&G; 81%/78% TSS	[23]
This study	$FeCl_3$	400 mg/L	99.2% O&G; 86% TSS	–

ones from the literature in Table 3. Furthermore, Bensadok et al. [21] found that ferric chloride does not allow an appreciable destabilization of an emulsion prepared from an oil A, whereas for an oil B, only the calcium chloride was effective.

In the second step, it was proceeded to the study of pH solution influence on the treatment in a range of 5.0–9.0, adopting the optimal concentrations determined in the previous phase. However, these studies were no longer performed for the less efficient coagulants (organic coagulant RIPOL 070 and inorganic salt $CaCl_2$). The pH is a very important factor to the coagulation/flocculation process using inorganic salts, since these compounds are converted into different ionic species as the pH value changes, thus influencing the coagulation. Fig. 4 shows that the best removals were obtained preferably at alkaline pH with the compounds RIFLOC 1815, $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3 \cdot 16H_2O$. The best TSS removal (72%) was obtained by using 400 mg/L of $Al_2(SO_4)_3 \cdot 16H_2O$ at pH 8.0. Regarding O&G and DOC parameters, the best removals (98.6% and 23%, respectively) were attained with 100 mg/L of $Fe_2(SO_4)_3$ at pH 8.0 and with 150 mg/L of RIFLOC 1815 at pH 9.0, respectively. Different results were reported by Guerrero et al. [24], who achieved maximum TSS removal efficiencies of wastewaters from fish-meal factories at pH 4 (97%) and 7.2–7.8 (75%) with sodium polyacrylate and chitosan, respectively. According to Al-Shamrani et al. [13] the best pH conditions for destabilization of an oil–water emulsion were found in the neutral pH range. Comparing our results with those obtained with other wastewaters, once again, as expected, it was verified that the optimum pH depends strongly on the nature of the wastewater to be treated and on the coagulant type. For example, a pH value of 8.35 has been reported as the optimum value for coagulation/flocculation treatment of pulp mill wastewater with aluminum chloride [25], pH values around 4.0 and 4.5 for palm oil mill effluent with chitosan, aluminum sulfate and polyaluminum chloride [26].

Looking at all the obtained results, it can be concluded that, as it was suspected, the best removals were achieved with inorganic salts (Table 2) rather than with organic polymers [17]. Additionally, the best results were observed in the tests carried out without wastewater pH correction and using $Fe_2(SO_4)_3$ and $FeCl_3$. As stated before $Fe_2(SO_4)_3$ is the best coagulant as far as

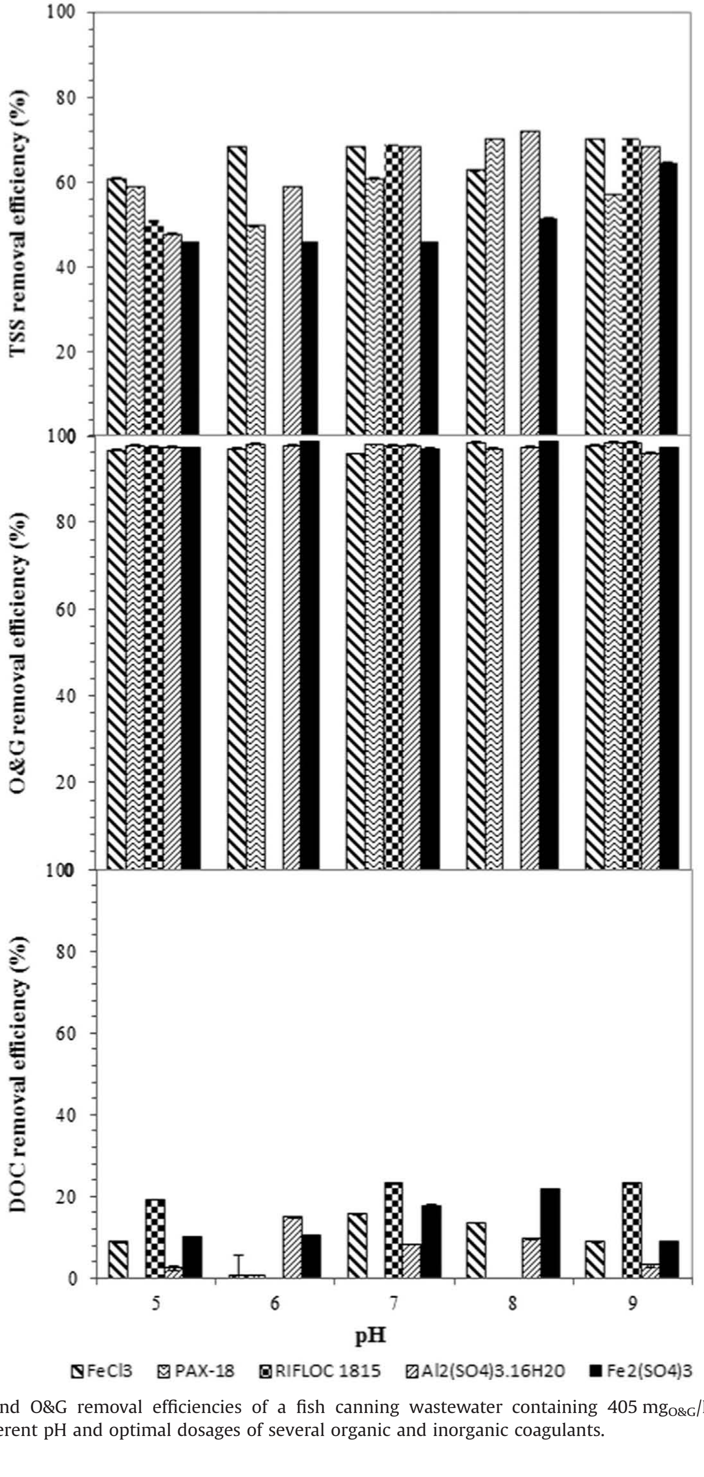

Fig. 4. TSS, DOC and O&G removal efficiencies of a fish canning wastewater containing 405 $mg_{O\&G}$/L, 350 mg_{TSS}/L and 471 mg_{DOC}/L at different pH and optimal dosages of several organic and inorganic coagulants.

O&G and DOC removals are concerned, whereas $FeCl_3$ should be used if one intends to maximize TSS reduction. However, the price is a key factor to decide what coagulant to select. To achieve similar removals of O&G, DOC and TSS it is necessary to employ 100 mg/L of $Fe_2(SO_4)_3$ and 200, 400 and 100 mg/L of $FeCl_3$, respectively. As the price of $Fe_2(SO_4)_3$ is about 240 EUR/ton and of $FeCl_3$ about 290 EUR/ton, the corresponding associated costs are 0.024 EUR/m^3 when using $Fe_2(SO_4)_3$ and 0.058, 0.116 and 0.029 EUR/m^3 regarding O&G, DOC and TSS removal, respectively, when using $FeCl_3$. Cost concerning sludge disposal was also estimated. Per each m^3 of effluent, 50 L of sludge with 1.18% of total solids is formed. After sludge dewatering using a belt filter press we get about 3 L of sludge with 20% of solids per m^3 of raw effluent. Considering that the dewatered sludge density is 1.2 ton/m^3, the amount of sludge to be disposed of is 3.6 kg/m^3 of raw effluent. The typical disposal cost of this waste in Portugal is 150 €/wet ton. Considering the effluent flow rate (10 m^3/day), the sludge disposal cost per day will be 5.4 €.

The results obtained for O&G removal efficiencies are comparable to the ones obtained by Ríos et al. [27] in the destabilization of cutting oil emulsions using inorganic salts as coagulants. They attained a percentage of oil removal greater than 90% with $CaCl_2$ and $AlCl_3$. Similar low results of DOC removal by coagulation/flocculation treatment of textile dyes wastewaters with inorganic salts were reported by Rodrigues et al. [28]. They achieved efficiencies of 40.3%, 17.7% and 27.6% of DOC removal in cotton, acrylic and polyester effluents, respectively.

3.4. Evaluation of flotation treatment

Fish canning wastewater pre-treatment was also studied by dissolved air flotation (DAF) after the sedimentation step. First, it was evaluated the influence of pressure variation in this treatment. For that, a pressure between 3.5–6 kg/cm^2 was applied for a constant recycle ratio (r) of 1. Recycle ratio is the quotient between the tap water volume in the pressure retention chamber and the wastewater volume in the flotation cell. The treated wastewater was analyzed in terms of DOC, TSS and O&G. Table 4 shows the results and it is possible to observe that the best O&G removal (83.3%) is attained at a pressure of 6 kg/cm^2. Regarding TSS removal, the efficiencies achieved were not very high, but it seems that with a pressure of 5 kg/cm^2 a somewhat higher removal was achieved (36.5%). Once again, as was observed with coagulation/flocculation treatment, dissolved air flotation showed also to be not effective in removing organic matter from fish canning wastewaters, since no reduction of dissolved organic carbon was observed. Looking at the results and taking into account that the maximum chamber pressure should not exceed the value of 6 kg/cm^2, it was decided to fix the pressure at the maximum chamber pressure value, since this is the pressure value that gives higher O&G removal and DAF is an appropriate method for removal of low density particles in suspension (such as oil and grease). In the next set of experiments, at optimum pressure, the recycle ratio was varied between 0.67 and 1.5. The treated wastewater was also analyzed in relation with TSS, DOC and O&G parameters and it was verified (cf. Table 4) that the higher removal values (43% of TSS and 94% of O&G) were reached at a recycle ratio of 0.67. Once again, no reduction of organic matter was observed at any of the recycle ratios studied.

To explain the performance of the flotation system, the air to solids (A/S) ratio was also determined. These values with the respective percent removal of O&G are shown in Fig. 5. Maximum A/S ratio of 0.058–0.087 kg air/kg O&G was observed for 6.0 kg/cm^2. The results also indicate that the removal efficiency of O&G increased with increasing A/S ratio up to approximately 0.09 kg air/kg O&G, achieving a maximum removal efficiency of 94%. After that it seems that the removal efficiency remains constant with further increase of A/S ratio.

The treatment of some oily synthetic wastewaters using DAF technique was already studied by Hanafy and Nabih [29] who achieved O&G removal efficiencies of 83% for cotton oil, 87% for corn oil and 90% for car oil with moderate oil contents. Increasing the oil concentration decreases the efficiency of separation for all types of studied oils. However, they found that the addition of a coagulant tends to improve the oil removal from wastewater. Rattanapan et al. [30] found also that DAF alone could not separate O&G from biodiesel production wastewater and acidification and coagulation were suggested as suitable treatment processes.

Table 4
TSS and O&G removal efficiencies of fish canning wastewater (350 mg_{TSS}/L and 405 $mg_{O\&G}$/L) by dissolved air flotation at different pressures and recycle ratios.

Pressure (kg/cm^2)	Recycle ratio (*r*)	Removal efficiency (%)	
		TSS	O&G
3.5	1.0	22.7 ± 0.8	64.6 ± 0.2
5.0	1.0	36.5 ± 0.2	77.4 ± 0.2
6.0	1.0	24.1 ± 0.1	83.3 ± 0.2
6.0	0.67	43.2 ± 0.2	93.5 ± 0.2
6.0	1.5	31.3 ± 0.1	85.7 ± 0.2

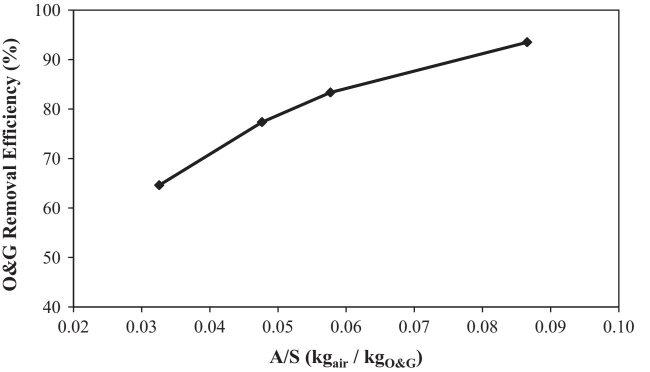

Fig. 5. O&G removal efficiency from a fish canning industry with 405 $mg_{O\&G}$/L as a function of *A*/*S* ratio in a DAF process.

3.5. *Evaluation of coagulation/flocculation + flotation treatment*

Several works in literature [31–33] indicate that air bubbles have a large negative zeta potential. This implies that the electrostatic repulsion makes attachment of a bubble to oil droplets unlike, unless the oil droplets are chemically treated. Thus, it is important to decrease the electrostatic repulsion barrier in oil emulsion systems prior to flotation. It is evident that the flotation of oil droplets that are stabilized depends on the physico-chemical properties of the system. Therefore, it is often necessary to make a chemical pre-treatment of the oil emulsion based on the addition of chemicals that destroy the protective action of the emulsifying agent and overcome the repulsion effect of the double layer, allowing the oil particles to form larger drops. Then, finally, an assay was made coupling the two treatment methods studied (coagulation/flocculation and DAF) in each one best conditions, in order to check if the removal would be better. In this case the formation of flocs would be promoted with the coagulant and then they may be separated from the aqueous phase by the attachment of the microbubbles formed at DAF.

Thus, first 400 mg/L of $FeCl_3$ were added to the decanted effluent and then, immediately after mixing, the effluent was subjected to the flotation process at a pressure of 6 kg/cm^2 and with a recycle ratio of 0.67. Using this treatment, removals of 41% of TSS and 96% of O&G were attained and, as in the DAF treatment, there was no organic matter removal. Comparing the results obtained with this solution with the ones achieved with the individual treatment methods, it is possible to conclude that with respect to removals achieved only with DAF, the coupling solution slightly improves the values of O&G removal achieved; however, it impairs the value of TSS removal. Nevertheless, the results for the studied parameters continue to be worse than the ones obtained only with the coagulation/flocculation treatment method even though it is necessary to add an additional compound (coagulant).

This way, it was found that the best method for removal of suspended matter from fish canning industries wastewaters is a decantation process for 1.5 h, followed by a coagulation/flocculation treatment with 400 mg/L of $FeCl_3$, leading to a treated wastewater with acceptable values for a subsequent secondary treatment, such as a biological process, for the removal of the organic material still present, making possible its reuse or the direct disposal into waterways.

However, the dissolved air flotation process combined with a previous stage of coagulation/flocculation showed to be a good solution for the treatment of cutting oil/water emulsion, allowing a noticeable improvement of the treatment effectiveness [21] and for soybean oil refinery wastewaters treatment, achieving removals of 73.6–92.9% of TSS and 94.2–99.8% of O&G [34], values much more similar to those obtained in the present study regarding fish canning wastewater treatment by coagulation/flocculation process.

4. Conclusions

Sedimentation, coagulation/flocculation and dissolved air flotation treatment processes were tested for primary treatment sequence of fish canning industrial wastewaters. Several parameters (sedimentation time, coagulant type and dosage, pH, chamber pressure and recycle ratio) were optimized to obtain maximum removal efficiencies. The best treatment system to remove the suspended solids of the wastewater in study was found to be a sedimentation step followed by coagulation/flocculation. Sedimentation for 1.5 h showed to be sufficient to achieve the maximum removals in terms of O&G and TSS (75% and 48%, respectively). The best results regarding the coagulation/flocculation treatment were attained using $FeCl_3$ as coagulant. With a coagulant dosage of 400 mg/L at raw pH wastewater, removal efficiencies of 99.2% of O&G, 85.8% of TSS and 25.2% of DOC were reached, leading to a wastewater with suitable characteristics to forward to a secondary treatment process for organic content removal and subsequent discharge. Flotation test has shown not to be a suitable primary treatment method for this type of effluents, even if coupled to a coagulation–flocculation process.

Acknowledgments

This work is partially supported by FCT – Fundação para a Ciência e a Tecnologia and FEDER under Programme COMPETE (Project PEst-C/EQB/LA0020/2013) and by project ValorPeixe – Valorização de Subprodutos e Águas Residuais da Indústria de Conservas de Peixe, project in co-promotion I&DT QREN, no. 13634, financed by FEDER through POFC – Programa Operacional Factores de Competitividade for which the authors are thankful. The authors also wish to thank the cannery in study for wastewater samples and Rivaz Química (Maia, Portugal) for kindly supplying the two organic coagulants. Raquel O. Cristóvão thanks FCT for the Pos-doc Scholarship (SFRH/BPD/81564/2011).

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