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Pollution prevention and wastewater treatment in fish canning industries of Northern Portugal

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Abstract. The main environmental problems of fish canning industries are high water consumption and high organic matter, oil and grease and salt content in their wastewaters. This work aims to analyze the situation (water consumption, wastewater production, wastewater characterization, etc.) of different plants located north of Douro river, in Portugal, in order to propose various solutions to their problems. Thus, initially it was made an identification and implementation of prevent and control pollution measures within the industrial units in order to reduce water consumption, minimize the wastewater production and reduce the pollutant load to treat. Then, the evaluation of wastewater treatability was started through a sedimentation and coagulation-flocculation process, with two organic coagulants (RIPOL 070 and RIFLOC 1815), commonly used in wastewater treatment. Sedimentation experiments showed that the flotation of 54% of oils and greases occurred, and 36% of total suspended solids were removed. The coagulation-flocculation process gave good results, especially in terms of oil and grease and total suspended solids removal. The best suspended solids removal efficiencies were 53% and 79%, using 400 mg/L of RIPOL 070 and 150 mg/L of RIFLOC 1815, respectively. At these dosages, both coagulants demonstrated excellent oil and grease removals, about 99% for RIFLOC 1815 and 88% for RIPOL 070.

Keywords: fish canning industry, wastewater treatment, integrated pollution prevention and control (IPPC), coagulation-flocculation.

1. Introduction

The canning sector is generally seen as the main segment of the fishing manufacturing industry at national level. In 1938 there were 152 canneries in Portugal which produced about 34,000 tons of canned fish. Currently there are 20 plants in operation producing 58,500 tons of canned fish [1] and seven of them are located north of Douro river.

The fish canning industry consumes a large amount of water in operations such as cleaning, washing, cooling, thawing, ice removal, etc. [2]. Consequently, this sector also generates large quantities of wastewater in which the treatment is particularly difficult due to the high content of organic matter and salts and to the significant amount of oil and grease they present [3]. These factors, together with the fact that these effluents present significant variations depending on the production process and on raw material processed, makes difficult to meet the emission limit values (ELVs) for industrial wastewaters (Decree-Law No. 236/98) and to deal with this problem in a sustainable manner. These effluents are often subjected to a pre-treatment before discharge to the sewage system for further treatment at an urban wastewater treatment plant. However, integrated pollution prevention and control (IPPC) measures should be implemented upstream in order to reduce the effluent volume and pollution load, eliminate, reduce or valorize certain

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hazardous substances [4], thus increasing the efficiency of water use (Decree-Law No. 173/2008). There is also a need, for both economic and environmental sustainability reasons, to consider the effluents treatment in order to obtain water with quality requirements that allow its reuse or recycling for industrial process [2].

This work aims to enable canned fish industries from northern Portugal to reorganize their production processes in order to make them more eco-efficient, through analysis and evaluation of their wastewaters, IPPC measures implementation and, finally, proposing wastewater treatment alternatives with the purpose of their reuse or recycling for the industrial unit. This study was initiated with chemical coagulation/flocculation and sedimentation treatments, using different coagulants commonly used in wastewater treatment.

2. Methodology

2.1. Analysis of wastewater characteristics

Five litres of wastewater from several fish canning industries from northern Portugal were collected. Standard methods for the examination of wastewater [5] were adopted for the measurement of total suspended solids (TSS), volatile suspended solids (VSS), total organic carbon (TOC), chemical oxygen demand (COD), biochemical oxygen demand (BOD), oil and grease (O&G), total phosphorus (P_{total}), total soluble nitrogen ($N_{total\ soluble}$) and ammoniacal nitrogen ($N_{ammoniacal}$).

2.2. Coagulation/Flocculation treatments

Before coagulation-flocculation treatment itself, a sedimentation test was made, where the effluent was left in graduated cylinders for a 2 hours period. 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 for jar tests were then analyzed in terms of TSS, TOC and O&G parameters. The wastewater characteristics before and after sedimentation test are shown in Table 2.

A standard jar test apparatus (Jar tester JLT6, VELP Scientifica) was employed for the coagulation-flocculation tests. Two different organic coagulants were tested: 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. In order to see if coagulant dosage influenced the wastewater treatment, several dosages were studied: 20-200 mg/L for RIFLOC 1815; 100-400 mg/L for RIPOL 070. Each jar was filled with 300 mL of sample from the sedimentation test and the coagulant dose for each jar was then added from a working solution of 1%. Then, the experimental procedure consisted of a rapid mixing at 150 rpm for 3 min and, after that, in order to form flocs, the wastewater was moderately stirred at 20 rpm for 15 min. Finally, a sedimentation stage allowed the flocs formed to settle. The supernatants obtained were then characterized.

These tests were all done with the same wastewater sample from fish canning industry A.

3. Results

3.1. Fish canning industries wastewaters characterization

The pollution load of fish canning industry wastewaters relies heavily on the type of fish being processed. Moreover, the volume and characteristics of the final effluent change significantly throughout the day, depending on the streams that are being launched: cooking effluents, effluents generated during sterilization, washing effluents, etc..

In order to obtain a representative set of information on water use and effluent production in fish canning industry, seven plants were identified at north of the Douro River in Portugal, referred in this work by the letters A to G. The typical value of water consumption in these industries was found to be approximately 15 m^3/ton raw fish, with global values of average daily consumption in the range of 20-300 m^3, depending on the plant capacity.

Some of the industries under study already have a pre-treatment of their effluents, such as a sieving and sedimentation in the case of company A, a treatment with a screw conveyor, a sieve and a flocculator in

company B and a filtering, retention and settling system in the case of company D. After these treatments, their effluents are discharged directly to the municipal wastewater sewage network. However, most of the time, these effluents do not meet the law requirements for their discharge. Table 1 shows the effluents characteristics from A, B and D industries, only after the pre-treatment that they have.

3.2. Integrated pollution prevention and control measures

The first step for implementing an integrated solution in a industry is to examine the possibilities to avoid and/or reduce waste at source through the application of cleaner production measures such as raw materials and technological changes, good manufacturing practices, etc.. Most of these preventive measures are easy to implement and have low costs. The application of these measures reduces the volume and the waste content, thereby allowing simpler and more economical waste treatment forms [6].

Since the fish canning sector consumes significant amounts of water, one of the main practices to be considered will be the implementation of measures aimed at reducing water consumption, such as: vacuum suction systems on the reception of raw materials; flow control in cleaning operations by installation of cutting devices; use of warm water or humid air to fish defrosting; use of ice removal tank supernatant for cooling hot water; reuse of scalling fish water, after filtration, in the initial fish washing; use of high pressure and low flow cleaning systems; use of compressed air instead of water when possible; reuse and water recycling from and to non-critical operations; collection of fish waste in closed containers to prevent losses; dry transportation of waste; adjusting the size of nozzles; etc..

Most of the water used in fish processing industries of this type results in an effluent with high content of suspended solids and high levels of COD/BOD, as shown in Table 1. The effluent have increased TSS due to the remains of fish, guts and sand and high COD and BOD_5 due to organic substances such as blood, soluble proteins and fish oil. It is therefore important to introduce measures aimed at reducing the pollution load of the effluent to be treated, such as: solid waste recovery; use of vacuum cleaners to clean the fish; blood and fish remains collection to prevent reaching the wastewater collector; installation of trays or other containers for solid waste collection, before falling on the pavement; adequate coverage of wastewater drainage canals, to minimize the entrainment of solid waste; etc..

Table 1: Wastewater composition of various industries of canned fish.

Parameter	Plant			
	A – Water from fish washing	A – Cooking water	B	D
pH	6.9	6.3	6.4	7.0
Conductivity (mS/cm)	4.7	20.2	4.0	12.5
TSS (mg/L)	324 ± 40		9407	650 ± 3
VSS (mg/L)	315 ± 44			598 ± 9
TOC (mg C/L)	639 ± 3			298 ± 3
COD (mg O_2/L)	1967 ± 26	21821 ± 176	17952	2053 ± 251
BOD_5 (mg O_2/L)	1546 ± 97		19200	1129 ± 85
Oils and greases (mg/L)	409	2146	2841	542 ± 50
P_{total} (mg P/L)	31 ± 1		67	16.6 ± 0.7
$N_{total\ soluble}$ (mg N/L)	211 ± 12			98 ± 21
$N_{ammoniacal}$ (mg NH_3/L)	3.2 ± 0.1			19.4 ± 0,6
NO_3^- (mg/L)	< Detection limit			< Detection limit
NO_2^- (mg/L)	< Detection limit			3,8
Cl^- (mg/L)	1874 ± 6			4146 ± 74
SO_4^{2-} (mg/L)	4.7			178 ± 84
PO_4^{3-} (mg/L)	< Detection limit			< Detection limit
F^- (mg/L)	7.0 ± 0.6			20.0 ± 10.3
Br^- (mg/L)	108 ± 4			74.5 ± 66.4

These pollution prevention measures are not the only ones possible for this industrial activity and also cannot be said that there is a unique solution applicable to all canned fish industries. The goal is to serve as a

starting point for technicians of the different industrial units in the definition of additional integrated pollution prevention and control measures.

3.3. Evaluation of coagulation-flocculation treatment

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 solids. The characterization of the clarified liquid is shown in Table 2. TSS, TOC and O&G reductions of, respectively, 36 %, 0 % and 54 % in relation to raw wastewater were obtained.

Table 2: Wastewater characteristics before and after sedimentation experiments.

	Wastewater	
	Initial	**After sedimentation**
TSS (mg/L)	396 ± 34	254 ± 14
TOC (mg/L)	427 ± 3	435 ± 3
O&G (mg/L)	759 ± 327	352 ± 81

This clarified liquid was then submitted to coagulation/flocculation tests. Two organic coagulant aids, RIPOL 070 and RIFLOC 1815, were tested at different dosages. These experiments were carried out at the pH of the raw wastewater. Table 3 shows a comparison of both coagulants effectiveness in removing TSS, TOC and O&G from the wastewater. The TSS and TOC data suggest a significant difference between the two coagulant aids. Maximum TSS removal (79 %) was achieved with a 150 mg/L dosage of RIFLOC 1815, whereas when 400 mg/L of RIPOL 070 was used, only 53% of TSS was removed. From Table 3, it is also possible to verify that increasing the concentration of RIFLOC 1815 from 20 to 200 mg/L, an increase in TSS removal is observed. However, this increase is not so pronounced for higher concentrations, tending to stabilize between 100-200 mg/L. Regarding the TOC removal, it is possible to observe that in the coagulant dosages studied, the RIFLOC 1815 coagulant can only remove up to 19 % and RIPOL 070 cannot get any removal of organic matter. This may be due to the fact that the coagulants themselves are organic materials, whose 1 % working solutions have high TOC levels (1555 mg/L for RIFLOC 1815 and 4748 mg/L for RIPOL 070). The use of high coagulant dosages may even contribute to the increase of wastewater TOC. The results in Table 3 show that both coagulants achieved excellent O&G removal efficiencies. The highest O&G removal (99.3 %) was obtained with 150-200 mg/L of RIFLOC 1815, leading to O&G values of 2.5 mg/L (approximately). The best removal observed with RIPOL 07 (400 mg/L) lead to O&G concentration of 42 mg/L. From all the situations studied, it was found that the highest removal efficiencies were obtained with RIFLOC 1815. This compound contains 18% of an inorganic salt (aluminum polychloride), which may have had some influence on the obtained results. Thus, in order to verify this assumption, future studies will include additional tests with the application of other potential coagulation/flocculation aids, such as inorganic salts. Additionally, the solution pH and mixing values may also be varied.

Table 3: TSS, TOC and O&G removal efficiencies obtained after addition of different dosages of RIFLOC 1815 and RIPOL 070 to the wastewater from the sedimentation test.

	Removal efficiencies (%)							
Coagulant dosage (mg/L)	**RIFLOC 1815**					**RIPOL 070**		
	20	**50**	**100**	**150**	**200**	**100**	**200**	**400**
TSS (mg/L)	51.8	49.8	75.6	78.7	74.0	31.5	34.6	52.8
TOC (mg/L)	7.2	8.5	15.7	18.5	18.7	0.0	0.0	0.0
O&G (mg/L)	98.4	98.2	98.9	99.3	99.3	85.8	87.1	87.9

This work showed the feasibility of using both sedimentation and coagulation-flocculation as operations to reduce significantly the content of suspended solids and oils and greases present in the wastewaters from fish canning industries. Further treatment of the clarified effluent could involve treatments such as flotation,

biological treatment, Fenton oxidation, reverse osmosis and UV radiation disinfection, looking to obtain water with characteristics that allow its reuse in the industrial process.

4. Conclusions

In this work an overview of environmental situation of fish canning industries in northern Portugal has been made, with the characterization of several industries wastewaters. In order to assist the industries in improving its production and environmental performance, a list of integrated pollution prevention and control measures to implement was proposed. Finally, the wastewater treatment by chemical coagulation/flocculation and sedimentation processes was evaluated, obtaining TSS and O&G total removal efficiencies of 86 % and 99.7 %, respectively, using 150 mg/L of RIFLOC 1815.

From the obtained results, it is possible to conclude that the sedimentation and coagulation/flocculation system is a good starting point for a treatment sequence for this type of effluents.

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