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Recovery of solved salts of the liquid effluents from the manufacture of cured hams: preliminary study

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ABSTRACT

Liquid effluents generated in the food industry can be treated by several separation processes to recover some components for possible reuse and/or valorization. This is done to further concentrate the volume of final waste to be managed. One of the industrial process in which this problem arises is the manufacturing of cured hams. In this process, hams are subjected to various steps including the addition of salt and subsequent desalting and washing with water, before the start of curing itself. This process generates a liquid effluent characterized by a high content of solved salts (mainly NaCl) and a variable amount of organic matter. Generally, this liquid effluent is dumped without being treated, causing environmental problems. The aim of this work is to find a proper treatment of the liquid effluent from the curing of hams, with the main objective of recovering the solved salts, as well as to minimize the liquid waste volume to manage. Some of the treatment techniques that could be applied to achieve these objectives are very usual in industrial effluent management: adsorption, chemical precipitation, ion exchange, evaporation, and membrane technology. The proposed treatment in this work consists of an appropriate pretreatment and subsequent treatment by membrane technology (salt preconcentration) and natural evaporation (concentration to solid state). Natural evaporation process takes place at ambient conditions, which brings a great advantage in terms of energy consumption, and it is based on the packing of wet surfaces exposed to the action of wind or forced ventilation, in order to increase the exposed surface per unit volume and to improve the productivity of the process. This paper presents the preliminary experiments carried out to characterize the liquid effluent from an industry of curing hams, and the treatment that has been tested to condition the effluent for further treatment by membrane technology and natural evaporation.

Keywords: Natural evaporation; Membrane processes; Valorization; Recovery; Cured hams

1. Introduction

The meat processing industry is very common to many countries and generates large volumes of wastewater. This liquid effluent requires considerable treatment in order to release it to the environment [1]. Generally, this treatment is a complex process which involves several steps. In most cases, pretreatment is necessary in order to improve the efficiency of the

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final treatment. The most common treatments in the meat processing industry are sedimentation, coagulation/flocculation and filtration as pretreatments, and membrane technology followed by disinfection/sterilization as final treatments [2].

One of the meat processing industries within this context is the cured ham manufacturing industry. Cured ham is industrially obtained by a process that can be slightly different according to the tradition of each production area, but the fundamental steps are the following ones:

- *Salting*: Hams are completely covered with a mixture of salt and additives and piled in cooled storage rooms (1–3.3℃) with a high air relative humidity (around 90%) for a period of time that depends mainly on ham weight [3].
- *Washing (desalting)*: After the salting period, hams are separated from salts, and before they enter the post-salting chambers, hams are conditioned in washing machines where rests of the salts are removed. Finally, hams are dried by these machines by means of a forced air flow.
- *Post-salting*: Once salts have been removed from ham surfaces, they go to post-salting chambers. Salt equilibrium takes place during this stage. Salt concentration is distributed inside the hams since after salting concentration is higher near the surface but very low in the deepest area. Hams are kept at low temperatures (around 3.3℃) for approximately 50 days.
- *Dry-maduration*: In this stage, there is a progressive loss of water; meanwhile, aroma and taste are developed thanks to enzymatic processes. Drying must be done progressively, beginning with temperatures between 10 and 12℃ and temperatures between 20 and 22℃ in the last month. The homogenized pieces of ham are placed in natural or air conditioning drying chambers, where the relative humidity usually varies between 70 and 90%, with a temperature range from 5 to 26℃. This period varies, according to the type of ham, from a minimum of 6 months to a maximum of 24 months [4].

In the course of curing process some liquid effluents are generated, mainly in the washing step in which several components (mainly NaCl and soluble proteins) are transferred from salted hams to desalting water [5]. Thus a liquid effluent is generated, which is characterized by a high salt concentration (dissolved salts and additives) and organic content (blood, fats, proteins, etc.).

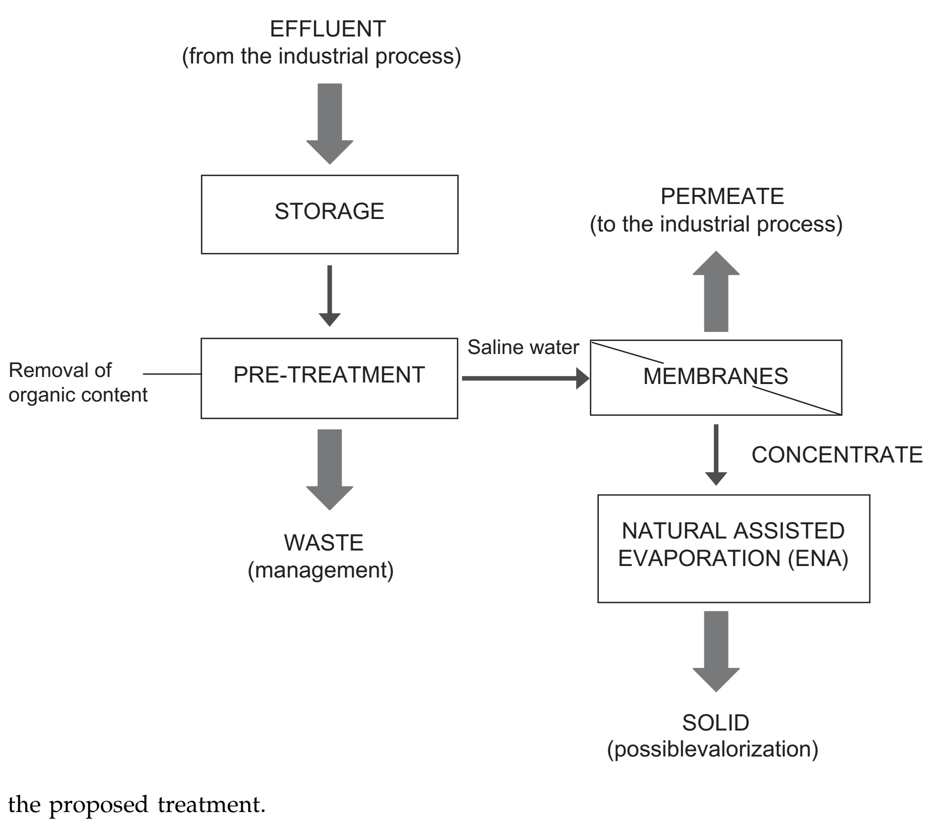

Fig. 1. Diagram of the proposed treatment.

In this work, we proposed a treatment for the liquid effluent from the desalting of hams that consists of the stages shown in Fig. 1.

The effluent from the washing of hams will be firstly stored before pretreatment with the aim of clarifying and conditioning the effluent for later treatment by membrane technology. Mainly, this pretreatment will consist of removal of organic content from the effluent. The pretreatment will produce a concentrated sludge, that must be properly managed, and a fat-free liquid stream. This liquid clarified in the pretreatment will be mainly composed of water and dissolved salts. This effluent will be treated in a membrane process where dissolved salts will be preconcentrated in the concentrate flow. The permeate of the membrane process will be water free from salts that will be able to be reused in the own industry. The concentrate flow from membranes will be finally treated in a Natural Assisted Evaporation (ENA) plant, where it will be concentrate to solid state.

ENA is a system based on capillary evaporation under ambient conditions, which has been already tested with hazardous wastes and with brines from brackish water desalination [6,7]. ENA system allows obtaining a solid concentrate that can be valued or which can contain components capable of being valued. Compared to conventional evaporation with heat supply, ENA system has the main advantage of working at ambient conditions, without the cost of producing thermal energy. In order to increase the productivity of the process, wet surfaces (in the form of clothes or capillaries) are exposed to the action of wind, so mass transfer surfaces would be enough to produce an adequate evaporation flux with minimal energy consumption.

In the proposed treatment, the application of ENA is aimed to concentrate the effluent treated by membranes to solid state. This final solid will be characterized to assess its possible valorization.

The objective of this work is to characterize the liquid effluent from the washing of hams and to define the required stages of pretreatment for subsequent treatment by membrane technology and ENA.

2. Materials and methods

This section describes the experimental methodology carried out to characterize the effluent and the physico-chemical experiments carried out to condition the effluent for further processing by membrane technology and natural evaporation.

2.1. Effluent characterization

Samples of real effluent were collected at the exit of the ham washing machine. Each sample was characterized by measuring the following parameters:

- conductivity (mS/cm),
- pH,
- temperature (°C),
- turbidity (NTU),
- suspension solids (mg/L), according to the standard UNE-EN 872, and
- dissolved solids (mg/L), according to the standard UNE 77031.

2.2. Physico-chemical tests

During sample characterization, different fractions of fat were observed in the effluent. To remove these fats, some physico-chemical experiments were carried out in order to improve the quality of the effluent before treatment by membranes and evaporation. The purpose of these experiments is to identify the most appropriate methodology for obtaining an effluent free of fats. Physico-chemical experiments performed are the following:

2.2.1. Centrifugation

Samples were filtered with a 0.05 mm filter. After this, the filtered samples were centrifuged during 30 min. The experiment was repeated adding different volumes of sodium hydroxide 0.1 M up to a rate of 1:3 of NaOH solution volume per filtered sample volume.

2.2.2. Sedimentation with NaOH

Samples were filtered with a 0.05 mm filter. After this, different volumes of sodium hydroxide 0.1 M were added. The solution was stirred 1 min with a magnetic stirrer and then it was allowed to settle. Then, the variation of turbidity with time was measured, every 15 min during 2 h, with the aim of observing the evolution of fat sedimentation with time.

2.2.3. Jar Test

A series of Jar Tests was carried out using three sands of different origin and quality, and adding NaOH in a range between 1 and 20 mL. In these tests, the order of addition was also studied to analyze its possible influence in the treatment. Once the chemicals were added, the turbidity was measured in each sample every 15 min for 1 h approximately.

Another series of Jar Tests was carried out in which the sands were added in a fixed concentration, the sodium hydroxide was added in the optimum concentration obtained in the previous tests, and polyaluminium chloride (PAC) was added in variable concentrations between 2 and 8 mL. Furthermore, all the possible orders of addition were tested. Once the chemicals were added, the turbidity was measured in each sample every 15 min for 1 h approximately.

3. Results

3.1. Effluent characterization

Table 1 shows the typical ranges parameters in the samples of effluent that have been characterized. As it can be seen in the table, the effluent to be treated has a high turbidity as well as high content of suspension solids. These high parameters involve the need of clarification before treatment by membrane technology. Furthermore, the content of dissolved salts is quite high, with values higher than 10,000 mg/L in some samples.

3.2. Physico-chemical tests

The main results of physico-chemical tests described are the following:

3.2.1. Results of centrifugation

In the centrifugation experiments, it was observed that fats were adhered to the walls of the tubes, but not with enough force since they easily slide. Furthermore, some fats were still in solution, so the performance of this process in fat removal is quite low. These reasons, besides the high operational costs of this process in the industry, motivate the rejection of this treatment line.

Table 1
Effluent characterization

Parameter	Range of variation
Conductivity (mS/cm)	3.36–16.15
pH	7.25–8.12
Temperature (°C)	18.2–24.6
Turbidity (NTU)	88.52–224.27
Suspension solids (mg/L)	121–2,564
Dissolved solids (mg/L)	3,780–10,500

3.2.2. Results of sedimentation with NaOH

Fig. 2 shows the evolution of turbidity with sedimentation time, for an experiment without any chemical and for an experiment with the addition of NaOH 0.1 M. As it can be seen, the addition of NaOH

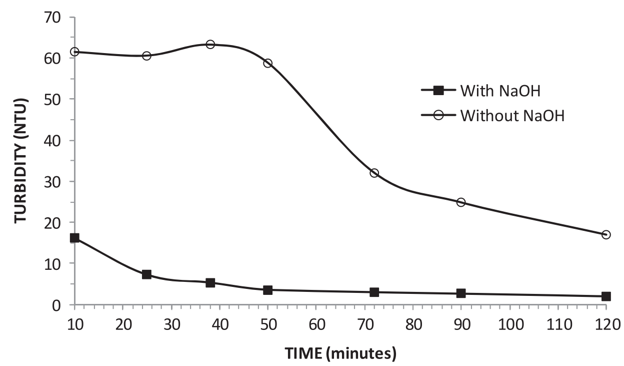

Fig. 2. Results of sedimentation with NaOH.

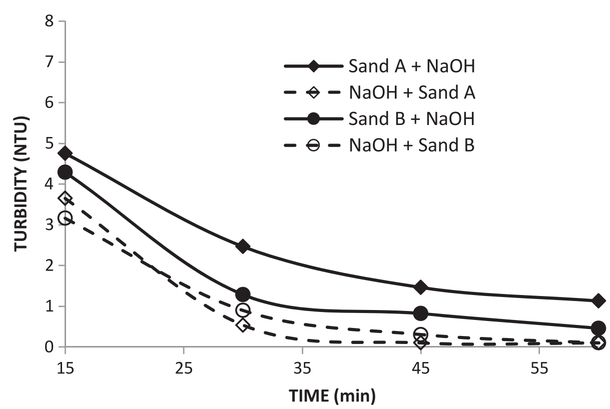

Fig. 3. Results of Jar Test with sands A and B with NaOH.

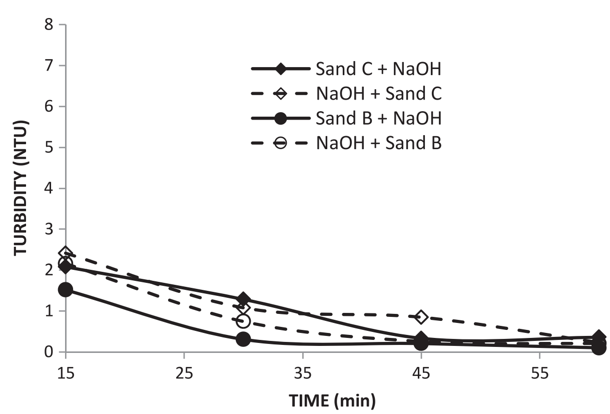

Fig. 4. Results of Jar Test with sands C and B with NaOH.

improves significantly sedimentation, since the turbidity reduce below 3 NTU in a period of time between 75 and 90 min.

3.2.3. Results of Jar Test

Figs. 3 and 4 show the best results obtained in the Jar Tests with sands and NaOH. In Fig. 3, sands A and B are compared in an experiment with the same effluent sample. The concentration of NaOH in these experiments is the one that performed the best results, corresponding to intermediate values of the tested range. Furthermore, two orders of addition are compared in the figure: first sand and after NaOH and first NaOH and after sand. Fig. 4 shows similar results for sand C and sand B.

Results of Figs. 3 and 4 show that sand addition (besides NaOH) highly improves turbidity removal in comparison with experiments carried out with NaOH. By means of sand and NaOH addition, turbidity is reduced below 3 NTU in a period of time around 25 min, in the more unfavorable case (sand A + NaOH). Except from this experiment, the turbidity was reduced below 1 NTU for periods of time around 30 min.

By analyzing the order of addition of sands and NaOH, it can be observed that results are significantly better when NaOH is added in first. With this addition order, time in which turbidity is below 3 NTU is substantially reduced to around 15 min.

From all the analyzed results, it can be stated that sand B, a bentonite type, is the one that produces better results in turbidity removal.

Finally, Fig. 5 shows the results of the series of Jar Tests, in which sand, NaOH, and different concentrations of PAC were added. As it can be seen in this figure, when PAC is added after NaOH and sands, turbidity removal is slightly improved. The period of time to reach turbidity values below 1 NTU is reduced to 15 min with volumes of PAC between 4 and 6 mL.

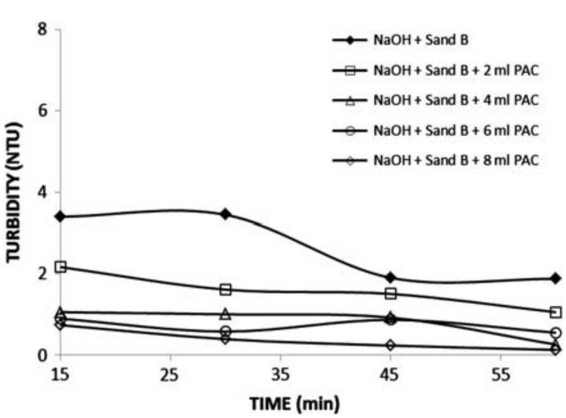

Fig. 5. Results of the Jar Tests with sand, NaOH, and PAC.

In spite of this improvement, it has been considered that there is no reason for using this chemical in the industrial process, because operational costs will increase significantly.

4. Conclusions

According to the analyzed results, the following can be stated:

- Experiments of centrifugation at maximum power have not been effective in reducing turbidity or fat removal.
- In the experiments of sedimentation with NaOH, it has been found that this chemical significantly improves turbidity removal, reaching turbidity values below 3 NTU after a period of time between 75 and 90 min.
- With the addition of NaOH 0.1 M and sands in the Jar Tests, it has been observed that turbidity is reduced below 3 NTU in 25 min time. This indicates the positive synergy of adding sand and NaOH in the stage of coagulation–flocculation. Furthermore, when NaOH is added before sands, this time is reduced to 15 min. In this case, turbidity can be reduced below 1 NTU in a period of time around 30 min.
- In the Jar Tests by using three additives such as sands, NaOH, and PAC, there has been a slight improvement in turbidity removal. However, this improvement does not justify the usage of PAC in the industrial treatment due to the increase in operational costs.

For all these reasons, after analyzing the results of present work, we consider that the results obtained in the Jar Tests with bentonite type sand and NaOH are the better ones according to the objectives of the pretreatment. The optimal observed concentrations of these chemicals will be taken as reference for designing the pretreatment installation for the liquid effluent of cured ham washing.

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