

## Treatment and Recovery of Brine Waters Coming from Agro-Alimentary Industries

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### ABSTRACT

The treatment of brine water currently represents one of the major problems in the disposal of waste produced by the agro-food industry. Brines mainly originate in food preparation and pre-treatment processes where the salt, whether in a solid state or diluted in water, is used as a preservative or as a dehydrating element. In Italy, the processing of cured ham represents one of the leading sectors of the agro-food industry. The thirty-one consortium companies located in the northern east Italy region, process around three million thighs of prosciutto a year. The salting phases and subsequent treatment in cold storage of ham legs, produce about 3500 tons / year of brine. The brine waters deriving from leachate obtained during the salting process have extremely high COD values (8,000 mg COD / l-12,000 mg COD / l) due to the presence of dissolved fat and blood, with salinity values salinity values averagely included between 60,000 mg NaCl2 / l and 150,000 mgNaCl2 / l, which make their treatment and recovery process extremely difficult. The results obtained during three years of the experimental study, allowed to highlight a high degree of purification of brine water together with the achievement of high sanitary hygienic characteristics of the recovered salt, which allow an enhancement of the product obtained with its placing on the market at extremely competitive prices.

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### Introduction

As part of research conducted in a region of North Eastern Italy aimed at identifying a possible treatment of brines in environmentally and economically compatible conditions, some types of brines coming from the agri-food sector and which currently represent a high complexity have been identified due to their chemical-physical characteristics. The areas of greatest brine production in the agro-food industry are mainly two, one in the canning industry and the second in the treatment of fresh meat. The canning industry generally has minor impacts on the environment, where the pollutants mainly derive from the washing of the machinery used in the production process during the brines preparation operations and where the treatment technologies are quite consolidated. In general, the main pollutant linked to the canning industry is the concentration of salt in the sewage, and of compounds linked to the washing process, such as, for example, surfactants, food preservatives, etc. The meat processing industry, on the other hand, represents greater environmental impacts and different problems in the treatment of the brines produced which are difficult to resolve. Only in the meat processing sector is the production of brine very high, some studies estimate a global production of brine equal to several tens of millions of cubic meters/years. The salting of fresh pork legs or other typical local products can take place in different ways depending on the various recipes used and handed down over time, with the result that the brines obtained have very variable chemical-physical characteristics both in terms of salt concentration, as well as other polluting compounds present such as COD, ammonia compounds, BOD and other organic elements. It remains clear that wastewater

treatment operations can prove very complicated where the technologies currently available are limited and very expensive in terms of energy. The presence of further significant quantities of polluting components considerably complicates the problem both from a technical point of view and from the point of view of management costs. Recent community legislation tends to significantly limit the disposal methods currently used, such as disposal at sea, disposal in surface waters, evaporation tanks, etc., significantly pushing towards the controlled treatment of brines in dedicated sites. This study, which lasted five years, focused its attention on identifying a solution that was both environmentally compatible and economically sustainable, where through a careful comparison of the technologies currently on the market we attempted to identify a systematic approach to the solution of the problem that combines greater conditions of management reliability connected to a high management economy.

### Materials and Methods

In the search for an environmentally and economically sustainable path the study has focused its attention on the production of brine waters which are particularly difficult to treat and in particular those deriving from the treatment of fresh meat, destined for a final maturing process in a controlled atmosphere, where the use of salt represents a fundamental element in the production process. Furthermore, the presence of important concentrations of other polluting fractions, such as blood, fats, and other compounds initially present in the meat which through osmosis are adsorbed in the salt fraction, are the main cause of the difficulties encountered in the brine treatment process, making this research a unique and very important case study from an environmental point of view. Table 1 shows the characterization of the solid salt used in the

salting process, highlighting the average weight characteristics of the product used in the meat salting process.

**Table 1: Chemical and Physical Characteristics of Sea Salt Used for the Production of Brine**

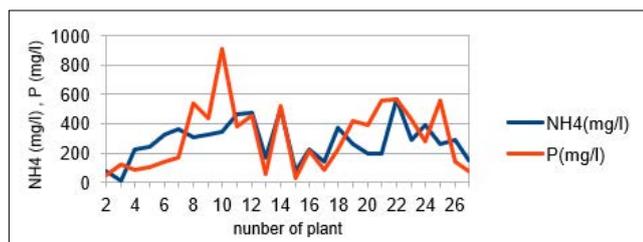
Material	Color	Granulometry	Umidity (%)	% di insolubility in water	NaCl (%)	CaSO4 (%)	Mg SO4 (%)	KC (%)I	MgCl2 (%)
salt	White/ grey	variable	4 - 7	0,4- 0,6	97 -98	0,3-0,4	0,1-0,2	0,1-0,15	0,3-0,4

Table (2) shows the average values obtained in the brine concentration by some food companies involved in the fresh meat treatment process. The values were calculated based on analyzes conducted over a five-year period. The graph in Fig. 1 represents the analytical values of the ammoniacal nitrogen and phosphorus present in the raw brine which make the treatment process particularly difficult. Again, from the Table 2, you can see the high content of organic and inorganic contaminants associated with these discharges. The average COD values calculated over a period of 5 years are equal to 15,437 mg/l, while the chloride content fluctuates on average between 80,000 mg/l and 150,000 mg/l. Based on the characterizations obtained from the analysis campaign, we proceeded with the creation of an experimental phase aimed at researching the best technology currently available on the market, highlighting the critical issues and any positive aspects deriving from their application in the brine treatment process, all in respect for high environmental efficiency and low economic impact.

**Table 2: Average Analytical Values of the Brine Disposed of - Weighted Average Calculated on the Basis of the Volumes Disposed of in the Last Five Years (2015 -2020)**

Parameter	u.m.	value
NaCl	g/l	103 (10,3%)
Chlorides	mg/l	62039
COD	mg/l	15437
NH4	mg/l	344
P	mg/l	435

Different experimental phases conducted both in the laboratory and on a pilot plant were implemented, which allowed the identification of the optimal characteristics that the treatment process must possess in order to ensure recovery of the solid fraction present in the brines and their possible reuse at within production processes, as well as the disposal of the liquid fraction in environmentally safe conditions.



**Figure 1: Analytical Averages of the Concentration of Ammoniacal Nitrogen (NH4) and Phosphorus (P) Present in Raw Brine Water, Coming from Different Plants**

The study was divided into two distinct experimental phases.

- A first phase characterized by a series of preliminary tests conducted both on a pilot plant and in the laboratory aimed at identifying the possible critical issues inherent to the type of technology that was intended to be adopted, identifying the methods and limits connected to its applicability for the specific case.

A second phase aimed at implementing the experimentally identified process that possesses the characteristics of technological, economic and environmental sustainability.

With these premises, the first experimental phase was divided into the following points:

- Evaluation of the optimal methods of equalization and homogenization of the raw brine obtained.

- Evaluation of the clarification treatment through the coagulation, flocculation and sedimentation phases, with the use of different coagulants and flocculants.

- Evaluation of the effectiveness of the final microfiltration and nanofiltration operations on both raw brine samples and clarified brine samples effectiveness.

- Evaluation of the evaporative process under vacuum, with the formation of

supersaturated brine, therefore, recovery and characterization of the condensation water and the solid fraction obtained by centrifugation on cloth.

The second experimental phase was characterized by a biological pre-treatment aimed at confirming and partially implementing the results obtained in the first experimental phase through the following tests:

- Feasibility of biological treatment with SBR type activated sludge plant of both raw brine and clarified brine,

- identification of the limits of applicability of the biological process to the identified brines, final ultrafiltration of the biologically treated brines and effluent characterization.

- Brine discoloration tests;

- Feasibility of the vacuum evaporative process, with formation of supersaturated brine, recovery and characterization of the condensation water and the solid fraction obtained with centrifugation on cloth.

For the analytical characterization of the parameters obtained during the laboratory and pilot plant tests, the APAT CNR IRSA methodology and the EPA methodology were used, where available. The coagulation, flocculation and sedimentation tests were conducted on homogeneous samples with a volume equal to 1 liter of raw brine. The microfiltration tests on the surnatant obtained in the chemical-physical pre-treatment process of coagulation, flocculation and sedimentation were conducted on a pilot plant operating in batches with the use of ceramic membranes with porosity equal to 0.45 microns (Fig. 2). The nanofiltration tests on the permeate obtained from the microfiltration process were conducted on a pilot plant operating in batch with the use of tangential flow polymeric membranes (0.2-micron cartridge

filter), with a controlled temperature between 28 °C and 35 °C. A high pressure pump (25 bar - 30 bar) ensured the recirculation of the brine within the nanofiltration system (Figure 3). Evaporation tests were conducted in the laboratory with Rotavapor on the sewage obtained from the microfiltration and nanofiltration tests (Figure 4).

**Figure 2: Physical Characteristics of the Membranes used in the Microfiltration Process**



Based on the data obtained from laboratory tests with Rotavapor, batch vacuum evaporation tests were carried out on a semi-industrial scale pilot plant (figure 5). the evaporation tests were conducted on two samples of 400 l each, of which the first sample consisted of brine clarified with Pac, the second of brine clarified with Pac followed by the nanofiltration process.



**Figure 3: Nanofiltration pilot plant**



**Figure 4: Rotavapor**



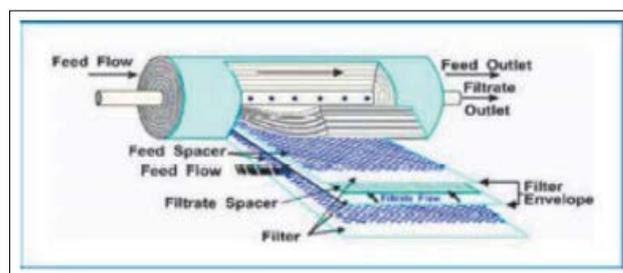
**Figure 5: Pilot plant for vacuum evaporation**



**Figure 6 -SBR Pilot plant for brine biological treatment**

For the experimental tests of brine treatment with a pilot plant of the SBR (sequencing batch reactor) type, a reactor with a volume of 25 liters was used, which represented a discontinuous operation aerobic activated sludge treatment system (figure 6).

Ultra filtration tests with tangential flow polymeric membranes (figure 7) were conducted on the supernatant fraction coming from the aerobic activated sludge pilot plant. In order to obtain a decolorization of the brine previously treated with a biological SBR system followed by ultrafiltration, some final tertiary treatment tests were conducted. The sewage samples were treated separately with activated carbon and on a pilot ozonation plant.



**Figure 7: Tangential Flow Ultra-Filtration Membranes**

In parallel with the studies on the treatability of the brine, some evaluations were conducted on the possibility of eliminating or at least limiting possible odorous emissions to the surrounding environment, coming both from the raw brine and during the subsequent treatment phases of the same.

### Results

Various coagulation and flocculation tests were conducted with Jar tests in the laboratory, on different types of brine (Table 3) even in very high salinity conditions (15%). The clariflocculation tests had the main purpose of highlighting some particular problems mainly due to the presence of high concentrations of chlorides and high values of protein material and fats present in the brines. The tests were conducted using various chemical coagulants currently on the market. These tests highlighted good treatability of the waste, with high removals of suspended solids present for some coagulants tested, guaranteeing good clarification of the final product. In other cases tested, the final product is still opalescent, due to the presence of partial coagulation probably due to a much stronger interaction between the material in suspension and the chlorides present in solution. From the various tests conducted it is clear the coagulation and flocculation pre-treatment, in which PAC (aluminum polychloride) or Sodium Hydroxide (Na OH) is used, leads to better results, with very rapid clarification times. Similar results, but with very laborious and expensive processes, are obtained using the Fenton reagent. The use of controlled

solutions of ferric chloride, ferrous sulphate, bentonites and other chemical compounds results in more opalescent final products (using FeCl<sub>3</sub> a reddish color is obtained), while with natural coagulants (bentonites), the clariflocculation process it does not lead to satisfactory results (probably due to the high salinity) and the weak interaction between the sodium bentonite particles and the suspended material. From Table 3, it can be observed that the use of PAC leads to a removal of total solids (SST) close to 99% (98.2%), and for Phosphorus (96.3%), obtaining a reasonable removal of COD initially present (60%). Chlorides pass almost unchanged in the removal process; smaller reductions are found for TKN (36.8) as well as for SO<sub>4</sub> sulfates (53%). On the basis of the results obtained, to consider the variability of the chemical-physical characteristics of the brine, a campaign of coagulation and flocculation tests was carried out on brines with different concentrations of contaminants, where only PAC (polyaluminium chloride) are used (Table 4).

**Table 3: Analytical Results from Chemical -Physical Treatment Test with Different Brines**

	pH	COD mg/l	Chlorides (Na Cl) mg/l	TKN mg/l	P tot mg/l	Sulfate mg/l	Oil & grease mg/l	Sst mg/l
Raw brine n° 1	6.3	12324	159932	929	321	386	20	857
Clarified brine with NaOH at pH 9	9.1	10783	144936	934	98	409	10	205
Removal %	na	12,9	na	0	69,5	0	50	76,1
Raw brine 2	6,6	9308	101764	778	451	501	10	500
Clarified brine with PAC	4,5	10764	107900	539	161	618	10	64
Removal %	na	na	na	18,1	64,3	na	na	87,2
Raw brine n° 3	6,6	9308	101764	778	451	501	10	500
Clarified brine with FeCl <sub>3</sub> – pH 9	4,4	8580	118200	539	3,5	772	10	85
Removal %	na	na	na	30,8	99,2	na	na	83
Clarified brine with n°4	6,6	9308	101764	778	451	501	10	500
Clarified brine with Fenton	7.0	7349	77800	459	36	3078	26	69
Removal %	na	21	na	41	92	na	na	83
Raw brine n°5	6,7	4195	104000	750	280	393	330	280
Clarified brine with PAC - pH 4,7	4,7	3640	105900	532	22	381	148	232
Removal %		13,2	na	29,1	92,1	3,1	12,9	29,7
Clarified brine with n° 6	5,7	11856	200197	1887	620	2054	40	2390
Clarified brine with PAC – pH 4,5	4,5	4680	194659	1193	23	996	10	42
Removal%		60,5	na	36,8	96,3	53	75	98,2

The tests have shown that with the clarification process it is possible to obtain an average reduction in COD equal to 38%, while for TKN and phosphorus average reductions equal to 30% and 68% respectively are obtained, with average reductions in total suspended solids by 64%.

Laboratory tests using microfiltration and nanofiltration membranes conducted on a pilot plant (Phase 1) on both pure and clarified brines, highlighted contrasting results and various critical issues. The tests conducted on a microfiltration pilot plant highlighted a rapid clogging of the membrane, and a consequent decrease in the specific flow (L/HM<sup>2</sup>), probably due to the formation of fats and/

or proteins on the surface of the membranes which, by forming a thin impermeable layer, limit the passage of the sewage. To limit this phenomenon, the brine was heated to values close to 40°C and the number of washings with both acidic and basic chemical agents of the microfiltration membranes themselves was increased. Also, in this case the results obtained proved to be fair but not sufficient for the intended purposes.

**Table 4: Analytical Results of Average Removal Obtained from Chemical-Physical Treatment Tests on Different Types of Brine Using only PAC (polyaluminium chloride)**

	pH	COD in mg/l	COD out (mg/l)	Cloruri (Na Cl) mg/l	TKN in mg/l	TKN out mg/l	P tot in mg/l	P tot in mg/l	Sst in mg/l	Sst out mg/l
Raw brine A	5,7	11856	4680	200197	1887	1193	620	23	2390	42
Raw brine B	6,7	4195	3640	104000	750	532	280	22	330	232
Raw brine C	6,1	8944	5096	101126	850	736	294	236	325	54
Raw brine D	6,5	4867	3266	101764	898	456	nd	nd	330	83
Raw brine E	6,1	16640	10192	208483	2273	1680	699	215	1860	55
Raw brine F	7,7	2101	1518	53010	433	337	167	60,9	nd	nd
Raw brine G	6,7	10348	5054	152741	nd	nd	nd	nd	nd	nd
Removal %	-	38,2		-	29,5		68,2		64	

In relation to the high volumes of brine to be subjected to the treatment and taking into account the large energy expenditure due to heating the brines and the consequent cleaning and restoration phases of the microfiltration membranes, the use of this technology in the pre-treatment phases was not recommended in the brine treatment. More satisfactory results were obtained with nanofiltration tests conducted in batches on different samples of clarified brine, using tangential flow polymer membranes. While highlighting better yields in the process of removing the organic and inorganic components present in the brines, in this case some critical issues have been highlighted. To carry out the tests, a preliminary acidification of the brines was carried out up to values close to pH 3- pH 4, to avoid precipitation phenomena of proteins and other organic materials present within the brine during the concentration phases. Also in this case, membrane clogging phenomena could be observed, however the occlusion of the membranes proved to be limited and reversible. At higher pH values, lower removal yields could be observed and, even when carrying out tests in which double passes were performed on the nanofiltration membrane, the results did not demonstrate better evidence than those that used a single pass.

The results obtained from the tests demonstrate various reductions in organic matter, but only in some cases was it possible to observe an acceptable final product (Table 5).

In any case, all the tests conducted in the laboratory and on a microfiltration and nanofiltration pilot plant have highlighted increasing management costs linked above all to temperature control and the use of chemical products for conditioning the brines before their treatment and for washing of the membranes, all these factors have led to not recommending this type of treatment for all the brines tested. The treatment of brine with high concentrations of sodium chloride on aerobic activated sludge biological systems has always proven to be a rather difficult approach, since it is known that chlorides in high concentrations have a strong inhibitory action on the biological activity of microorganisms (in the bibliographic limit is equal to 8%).

**Table 5: Values Obtained from a Series of Nano-Filtration Tests on Brine Clarified with a Pilot Plant**

	pH	COD mg/l	NaCl mg/l	N total mg/l	P totale mg/l	Sulfate mg/l	SST mg/l	Oil & grease mg/l
Clarified references brine - 1	4,5	4680	194659	1193	23	996	10	42
Brine 1 after nano-filtration	4,5	2531	193369	510	9	21	4	<10
Reduction %		45,9	--	57,3	60,9	97,9	60	100

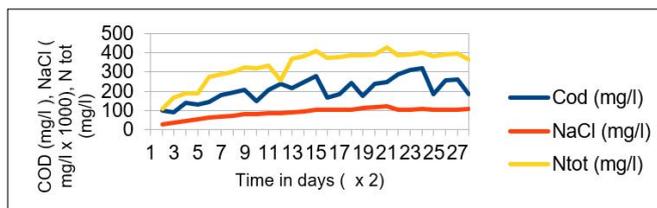
Clarified references brine - 2	5,7	7436	154724	837	291	110	178	4
Brine 2 after nano-filtration	8,9	6275	108900	164	0,03	205	77	<10
Reduction %		15,6	29,8	80,4	100	nd	56,7	100
Clarified references brine - 3	4,5	10764	107900	637	161	618	10	64
Brine 3 after nano-filtration	4,8	1040	88200	252	<0,001	<10	52	22
Reduction %		90,3	18,2	60,4	100	100	nd	65,6
Clarified references brine - 4	4,7	3640	105900	532	22	381	232	148
Brine after nano-filtration	4,9	1602	91000	274	<0,001	<10	63	46
Double pass nano - filtration	5,7	520	110724	207	<0,001	<10	4	<10
Reduction %		85,7	--	61,1	100	100	93,8	100

The tests with the SBR reactor were conducted using a small quantity of previously acclimatized sludge (activated sludge deriving from the purification of whey), then following a further acclimation phase, adding increasing quantities of brine concentrations to the subjected sewage per treatment, until sodium chloride concentrations close to the biological reactor of 12% - 15% are reached.

With the pilot plant consisting of the SBR type activated sludge biological reactor, some tests were conducted using three different types of brine and concentrations of sodium chloride:

- Pre-treated brine with a NaCl concentration of 10%.
- Raw brine with a NaCl concentration of 10%.
- Raw brine with a NaCl concentration of 12% - 15%

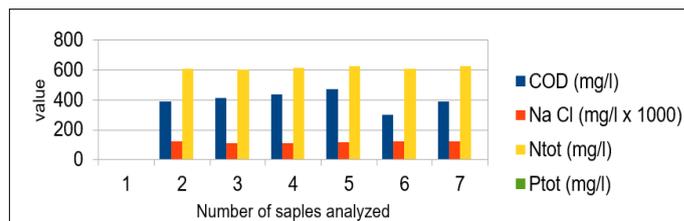
The tests were conducted over a period of approximately 6 months, the data obtained highlight a good acclimatization phase of the bacterial flora (probably favored by the high presence of organic substance which led to its deterioration over time), furthermore these data highlight that once the concentration of sodium chloride (NaCl) is close to 10% - 12%, the biomass is rather stable over time, presenting COD removal yields close to 92.4%. The average reduction percentages of nitrogen and phosphorus reach 17.6% and 99.5% respectively (Figure n. 8).



**Figure 8:** Brine Treatment Tests with Biological Activated Sludge on SBR Plant

In order to favor both the growth of the bacterial micro flora and the sedimentation process, various chemical adjuvants were used;

these contributions highlighted an agglomerate of the bacterial flora, a greater resistance to salinity and a good effect in the static sedimentation phase of the biological sludge



**Figure 9:** Brine Treatment Tests with Activated Sludge on SBR whit NaCl Concentration of 120.000 mg/l

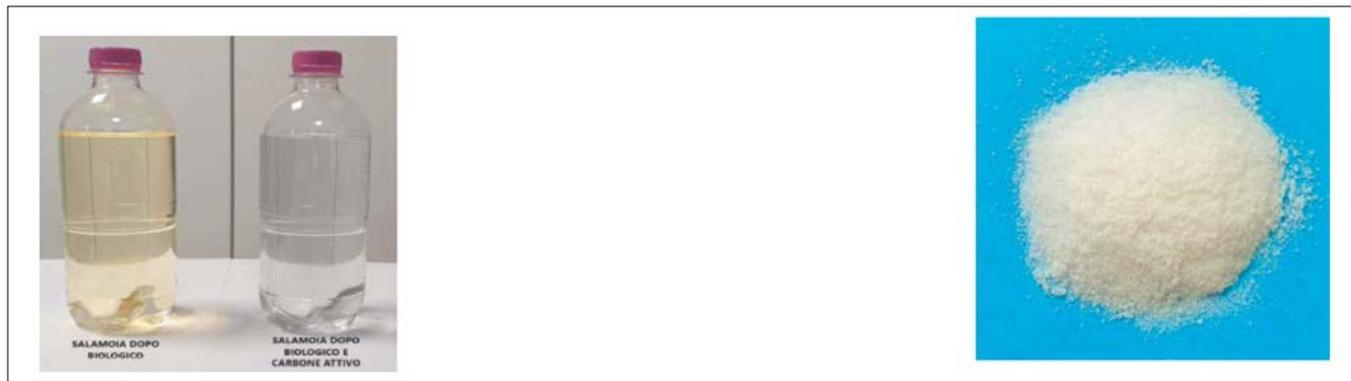
On the supernatant coming out of the biological treatment after static sedimentation, several pilot-scale tests of membrane microfiltration with tangential flow were conducted (Tab. 6).

**Table 6: Average Values Obtained from a Series of Micro Filtration Tests on Brine from with Biological Pilot Plant.**

	pH	COD mg/l	Chlorides (Na Cl) mg/l	N total mg/l	P tot mg/l	Sst mg/l
Brine in.	9,1	10738	144936	934	409	205
Brine after micro filtration	5,7	7436	154729	837	110	178
Reduction %		30,7	na	10,4	73,1	13,2

On samples of brine treated with an SBR-type activated sludge system after micro filtration (to separate the solid fraction from the liquid one), some vacuum evaporation tests were conducted both a laboratory system (Rotovapor) and on a pilot plant of larger. The tests had the aim of separating the salt fraction in the form of

crystals from the liquid fraction, verifying that both phases were environmentally compatible with a view to environmental recovery.



**Figure 10:** Brine from Biological Treatment after Ultra Filtration Figure n.° 10 - Salt Recovered after the Vacuum before and after Treatment with Activated Carbon Evaporation Phase and Subsequent Filtration

The main problem to be faced after the microfiltration phase was represented by the high presence of ammoniacal nitrogen in the brines. Two different experiments were analyzed, the first of which involved steam stripping of the nitrogen present in the brine, the second a conditioning phase at values lower than neutrality with strong acids. The first option was discarded in relation to the plant and management complexity, and the unreliability of the removal yields that could be obtained over time. The second, although economically questionable, and taking into consideration the fact that at a high pH, the nitrogen present in the brine is in the ammonia form, while at an acid pH the nitrogen is in the salified form of ammonium ion (low evaporation even at temperatures relatively high), evaporation tests of the brine were carried out at different pH values, in order to limit the concentration of nitrogen in the condensates, and therefore allow the disposal of the liquid fraction in environmentally safe conditions.

Table 7 shows the results after evaporation obtained from tests conducted on the brine; these values highlight that by acidifying the brines up to values close to five it is possible to obtain a condensate in which the concentration of nitrogen in its various forms is negligible and in line with the environmental parameters required for its discharge into the sewer.

**Table 7: Results Obtained from Vacuum Evaporation Tests from Brine Biologically Treated Microfiltered, Chemically Conditioned at Different pH Values.**

	pH	Conductibility (μ S/cm)	COD mg/l	Chlorides (mg/l)	P tot (mg/l)	NH4 (mg/l)	Total N (mg/l)
Clarified brine biologically treated - micro filtrated	7,8	na	244	86116	1,34	318	na
Condensate from evaporated brine at pH = 7,8	9,9	240	5	10,8	0,19	nd	56
Condensate from evaporated brine at pH = 10	10,2	361	<20	22,9	nd	201	210
Condensate from evaporated brine at pH = 5	9,1	222	<20	22,1	nd	4,35	5

Before the evaporative phase, the brines obtained were treated both with activated carbon and through controlled ozonation processes (Figure 9), which allowed a completely white salt to be obtained after evaporation, free of any chromatic trace (Figure 10).

The results of the tertiary treatment tests conducted on the brine are reported in Tab. 8, highlighting a good capacity for removing the color initially present, while the color removal tests, which saw the use of ozone, demonstrated a lower performance.

**Table 8: Results Obtained on Brine Samples After Micro Filtration and Biological Treatment with Activated Carbon**

	Activated carbon gr/l	COD mg/l	NaCl mg/l	N tot mg/l	P Tot mg/l	Sulfate mg/l	Oil & grease mg/l	Color
Brine A	Tal quale	364	104507	548	2,1	591	22	Light Yellow
Brine A with a.c.	1	333	105748	524	5,48	608	15	colorless
Reduction %	na	8,50%	na	4,30%	n.a	n.a	n.a	100
Brine B	Tal quale	333	101220	598	2,69	598	104	Light Yellow
Brine B with a.c.	4	260	100911	n.a.	12	n.a.	104	colorless
Reduction %	na	21,9	na	4,8	n.a	n.a	n.a	100
Brine C	Tal quale	302	102793	570	2,16	595	120	Light Yellow
Brine C with a. c	4	260	99535	563	12,2	607	103	colorless
Reduction %	na	13,9	na	1,2	n.a.	n.a.	n.a.	100

From the vacuum evaporation tests conducted with a pilot plant, a micro crystallized salt free from any impurity was obtained, which is well suited to being placed on the market.

A series of chemical-physical analyzes were conducted on this salt aimed at its characterization. The analyzes on the solid salt obtained after evaporation and subsequent centrifugation are reported in Table 9 and Table 10 where the optimal qualitative characteristics of the salt obtained from the brine treatment and recovery process are highlighted.

**Table 9: Granulometric Characteristics of the Salt Obtained from the Evaporative Process of the Brine Treated with Activated Sludge with SBR and Micro Filtered.**

Parameter	Humidity	Residue at 105 °C	Titolo (NaCl)	Grease	N total	Insoluble in H2	Residue in H2O org. mat.	Total microbial load
U.M.	% (p.p)	% (p.p)	% (p.p)	% (p.p)	% (p.p)	% (p.p)	% (p.p)	% (p.p)
Salt from brine recovery	5,2	94,8	99,8	0,1	0,04	< 0,01	< 0,01	<10

**Table 10: Chemical and Microbiological Characteristics of the Salt Obtained from the Evaporative Process of the Brine Treated with Activated Sludge with SBR and Micro Filtered.**

Granulometry (mm)	U.M.	Salt coming from brine evaporation (%)
<0,16	% (p.p)	4,4
> 0,16 - <1	% (p.p)	68,6
>1 - < 3	% (p.p)	26,7
>3 - < 4	% (p.p)	0,2
>4 - < 5	% (p.p)	0,1
> 5	% (p.p)	< 0,1
Total halophilic microbial load	% (p.p)	<10

**Conclusions**

The results obtained in this study concerning the technical-economic evaluation conducted with the best technologies currently available on the market for the treatment and recovery of brines, have led to the identification of a set of complementary technologies which, if appropriately applied, can definitively resolve the brine treatment and recovery process in safe and environmentally sustainable conditions and with economically acceptable costs. The operations of good homogenization and initial chemical pretreatment followed by a further chemical-physical pretreatment phase are a condition considered essential for the subsequent recovery phases, as they eliminate the most

refractory component and inhibit the proliferation of odorous formations which can represent a serious environmental problem during subsequent purification operations. First of all, low concentrations of sodium hypochlorite (NaClO) on the sewage subjected to homogenization, strongly limit the proliferation of odors in all the initial and subsequent steps in the treatment and recovery operations of the brines. It has been observed that the use of coagulants containing aluminates (PAC) are more effective than other types of chemical coagulants (NAOH, FeCl3 etc.) or natural coagulants (bentonites, etc.). The activated sludge process, followed by an ultrafiltration phase on membranes, proved to be the simplest, most reliable and with decidedly acceptable costs

when compared with other treatment systems applied on raw and/or clarified brines (micro-ultrafiltration, nano-filtration, reverse osmosis). This phase, if appropriately monitored, is able to remove a large part of the organic substance present even with extremely high salinity concentrations (NaCl content >12% - 15%). The main problem in using removal systems with membranes is represented by the formation of blockages due to fats and proteins on the surface of the membranes themselves, and the presence of high salinity which amplifies the phenomenon, causing a sudden collapse in removal yields. Even if the clogging of the membranes is reversible, the costs for their efficient use are generally high, mainly linked to the heating of the brines and the consistent use of chemicals for their washing. Before proceeding with the vacuum evaporation phase, aimed at recovering the solid salts and condensates, it is advisable to proceed with a further clarification phase through the use of activated carbon, given the presence of nano-colloids within the brines which pass practically unchanged during the ultrafiltration process, if not previously eliminated they can have a strong visual impact on the final recovered product. The use of modest quantities of activated carbon in the clarification process is preferable to any treatment with ozone, as it is easy to apply and has less impact from a management point of view. The high salinity concentrations recommend the use of a more reliable process than an osmotic process (see above). The study confirmed the vacuum evaporation process as a valid alternative which, although involving significant energy costs, guarantees efficient recovery of the salt fraction by presenting excellent chemical-physical and microbiological characteristics, allowing its possible commercialization on the market. Furthermore, the use of the evaporative process gives the condensates obtained

characteristics in line with the most stringent environmental safety regulations, and effective control in the process of removing the nitrogen component generally associated with the organic substance present, which represents a highly critical issue, and problems that are not easy to solve [1-6].

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