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Review

Treatment of organic pollution in industrial saline wastewater: A literature review

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A B S T R A C T

Many industrial sectors are likely to generate highly saline wastewater: these include the agro-food, petroleum and leather industries. The discharge of such wastewater containing at the same time high salinity and high organic content without prior treatment is known to adversely affect the aquatic life, water potability and agriculture. Thus, legislation is becoming more stringent and the treatment of saline wastewater, both for organic matter and salt removal, is nowadays compulsory in many countries. Saline effluents are conventionally treated through physico-chemical means, as biological treatment is strongly inhibited by salts (mainly NaCl). However, the costs of physico-chemical treatments being particularly high, alternative systems for the treatment of organic matter are nowadays increasingly the focus of research. Most of such systems involve anaerobic or aerobic biological treatment. Even though biological treatment of carbonaceous, nitrogenous and phosphorous pollution has proved to be feasible at high salt concentrations, the performance obtained depends on a proper adaptation of the biomass or the use of halophilic organisms. Another major limit is related to the turbidity problems inherent in saline effluents. For this reason, the major need for research in the future will be the combination of physico-chemical/biological treatment of saline industrial effluents, with regard to the global treatment chain, in order to meet the regulations.

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1. Introduction

The economic importance of salt (NaCl) is huge in regard to its consumption that exceeds 30 million tons per year in the European Union. The main end markets for salt are the chemical industry (mainly the chloralkali sector), road de-icing and agro-food industries. Other non-negligible uses of salt are found in the petroleum, textile and leather industries as well as for softening hard water. All these sectors generate very large amounts of saline wastewater, rich in both salt (NaCl) and organic matter. When this wastewater is discharged into the environment without prior treatment, it can cause severe damage by contamination of soil, surface and groundwater.

Concerning the environmental dimension of the problem of salinification, the European Union Directive 2000/60/EC establishing a framework for Community action in the field of water policy requires measures to prevent adverse impact from saline pollution (European Union, 2000). For inland freshwater, salinity is one of the parameters which must be considered in relation to any body of water, and member States are required to set standards in order to ensure the viability of the ecosystem and the maintenance of a biological community deviating only slightly from that normally associated with the ecotype when conditions are undisturbed. Thus, under Article 11 of the Directive, member States have to establish measures to ensure that those standards are observed.

Faced with tightening regulations, the interest in saline effluent treatment processes, both for salt and organic matter removal, has been increasing rapidly over the last 10 years. Saline effluents are usually treated through physico-chemical means, as conventional biological treatment is known to be strongly inhibited by salt (mainly NaCl). However, physico-chemical techniques are energy-consuming and their start-up and running costs are high. Nowadays, alternative systems for the removal of organic matter are studied, most of them involving anaerobic or aerobic biological treatment. Thus, the purpose of this review is to: (1) list the major industrial sectors generating saline effluents, (2) summarise the latest advances in saline wastewater treatment processes, emphasising biological treatment, (3) focus on combined aerobic/anaerobic treatment processes for carbon, nitrogen and phosphorus removal, (4) focus on the specific problem of turbidity encountered in most of the cases, (5) discuss the relevance of combined treatments for saline industrial effluents, within the context of the global wastewater treatment chain.

2. Industries generating saline effluents

2.1. *Food-processing industry*

The salt destined for human consumption (NaCl) has a double role: for nutrition and for food conservation. The agro-food sectors requiring the highest amounts of salt are meat canning, pickled vegetables, dairy products and the fish processing industries. Salt is known to reduce the water activity and therefore constitutes a microbiological agent of stability (Lozach, 2001). In the food industry, saline effluents are mainly generated by the use of brine solutions and dry salt (NaCl) for obtaining the finished product. We will focus in this paper on two sectors of the agro-food industry that generate high amounts of saline effluents, i.e. the pickled vegetable and the fish processing industries. In the pickled vegetables industry, the main source of saline pollution is related to the use of brine for canning and pickling. Consequently, the brine losses and rejections pollute the wash water. Olive oil mills, in particular, reject great quantities of saline wastewater (Vitolo et al., 1999). In the fish processing industry, the sources of pollution are initially related to the unloading of fish accompanied by seawater. The fisheries then generate wastewater rich in proteinic nitrogen, organic matter and salts (Antileo et al., 1997).

2.2. *Leather industry*

The tanning process, which turns raw hides and skins into finished leather products, is a lengthy process that involves several steps, many of which requiring the addition of salt (Lefebvre et al., 2005). The potential environmental impact of tanning is significant. The tanning process is almost wholly a wet process that generates very large amounts of wastewater. Certain streams are hypersaline, such as the pickling and the chromium tanning effluents or the soak liquor generated by the soaking of hides and skins that can contain as much as $80\,g\,l^{-1}$ of Nacl.

2.3. Petroleum industry

Crude oil is a complex mixture that contains mainly aliphatic, alicyclic and aromatic hydrocarbons (Rincon, 2002). The refining process requires de-emulsifiers and the waste water (called production water) resulting from the decantation of the oil–water emulsion presents a broad range of salinity, from fresh water up to three times the salinity of seawater and beyond (Diaz et al., 2002).

3. State-of-art of the treatment applied to saline effluents

3.1. Physico-chemical treatment of hypersaline effluents for the removal of salt and organic matter

Hypersaline effluents are often recalcitrant to biological treatment; consequently, physico-chemical treatment is generally required to remove the organic matter as well as the salts from such effluents. The main technologies that have been investigated are evaporation, coagulation–flocculation, ion exchange and membrane techniques.

3.1.1. Thermal techniques

Solar evaporation is a low-cost technique commonly applied to concentrate the salts and organic content of saline effluents, thereby reducing the volume of effluents. In the leather industry, the hypersaline soak liquor generated by the soaking of hides and skins is sometimes segregated from the other streams because of its high salt content and sent to solar evaporation pans (Lefebvre et al., 2005). However, the reuse of the solid salt thus obtained is made impossible due to its high degree of impurity. Modern technologies include multiple-effect evaporators (MEE), in which water is boiled in a sequence of vessels, each held at a lower pressure than the previous one. Because the boiling point of water decreases as pressure decreases, the vapour boiled off in one vessel can be used to heat the next, and only the first vessel (at the highest pressure) requires an external source of heat. Economic analysis showed that MEE could be competitive with other desalination processes (mainly reverse osmosis, RO) in regions with low energy cost, especially in the Gulf countries (Morin, 1993; Wade, 1993).

3.1.2. Coagulation–flocculation

Although not efficient for salt removal, coagulation–flocculation can be used as a pretreatment of hypersaline effluents to remove their colloidal COD. For instance, Ellouze et al. (2003) studied colloid coagulation in cuttlefish-transformation effluents, using aluminium sulphate ($165.5\,mg\,l^{-1}$) followed by a flocculation step using MgO ($750\,mg\,l^{-1}$) and poly-dimethyl ammonium chloride ($35\,mg\,l^{-1}$). The coagulation–flocculation of this effluent made it possible to reduce the turbidity and the COD of the effluent by 7 NTU and 90%, respectively.

3.1.3. Ion exchange

Ion exchange is a commonly used technique to soften hard water and to demineralise water (Metcalf and Eddy, 2003). Ion exchange resins contain fixed cations or anions capable of reversible exchange with mobile ions of the opposite signs in the solutions with which they are brought into contact. For salt reduction, both anionic and cationic exchangers must be used. The wastewater is first passed through a cation exchanger where the positively charged ions are replaced by hydrogen ions. The cation exchanger effluent is then passed over an anionic exchanger were the anions are replaced by hydroxide ions. Thus, salts are replaced by hydrogen and hydroxide ions to form water molecules. Following this service cycle, the process involves a regeneration cycle in which the exhausted resin is backwashed to remove trapped solids. The main problem of applying ion exchangers to wastewater treatment is a high influent suspended solids concentration that can plug the resin, causing inefficient operation. Another problem is that ion exchangers require costly regenerant and produce troublesome waste streams (McGhee, 1991).

3.1.4. Membrane techniques

Membrane techniques consist in the transfer of selected molecules under the effect of a concentration or pressure gradient, or an electrical field. Although not suitable for salt removal, ultrafiltration (UF) can be used for the removal of suspended solids and colloidal COD in saline effluents, as already noted by Afonso and Bórquez (2002) who used UF to concentrate and recycle the proteins contained in seafood-processing wastewater. In the same study, a reduction of abundant suspended solids clogging membranes was obtained by a preliminary microfiltration step. The combination of centrifugation and UF steps also achieved the elimination of 90% of the COD as well as the separation of grease in saline olive oil processing effluents (Turano et al., 2002).

For salt removal, suitable membrane techniques include electrodialysis and reverse osmosis (RO). In the electrodialysis process, water flows between alternately placed cation permeable and anion permeable membranes (Metcalf and Eddy, 2003). A direct electric current provides the motive force for the ion migrations through the membranes. Water in alternate cells becomes weak in ions due to migration of ions under electric potential and other cells become concentrated in salt ions. RO is a process in which water is separated from dissolved salts in solutions by filtering through a semi-permeable membrane at a pressure greater than the osmotic pressure caused by the dissolved salts in the wastewater (Metcalf and Eddy, 2003). It is the most efficient and most commonly used process in desalination, allowing the removal of monovalent ions such as NaCl. RO has the advantage of removing dissolved organics that are less selectively removed by other demineralisation techniques. The primary limitations of RO are its high cost and the limited operating experience in the treatment of domestic and industrial wastewater. Yet, Schutte et al. (1987) described the operation of two South African large scale plants treating power plant effluents, one operating with electrodialysis and the other with RO. In relation to olive oil processing effluents, RO also ensured the elimination of 99.4% of the salts and 98.2% of the

COD, as well as complete elimination of the colour and the BOD_5, with a transmembrane pressure at 55.2 bars and a flux of $52.5\,l\,m^{-2}\,h^{-1}$ (Sridhar et al., 2002). Finally, it is important to note that a very high-quality feed is required for efficient operation of a RO unit, as membrane elements in the RO unit can be fouled by colloidal matter in the feed stream. For this reason, UF is usually considered as the most suitable pretreatment for RO and some studies have been devoted to the combination of UF/RO for olive oil effluent treatment (Vitolo et al., 1999).

3.2. Aerobic treatment of saline effluents for the removal of organic matter

3.2.1. Effect of salt on aerobic treatment

High percentages of salt are known to compromise the correct operation of conventional aerobic wastewater treatment processes above chloride concentrations of $5–8\,g\,l^{-1}$ (Ludzack and Noran, 1965). In spite of the detrimental effect of salt on microbial activity, moderate acclimation of activated sludge to high salinity is possible. Acclimation implies the exposure of non-salt-adapted micro-organisms to increasing salt concentrations in order to permit the obtention of satisfactory effluent treatment performance at a given salt concentration. The success of such adaptation depends on several factors, such as the type and growth phase of micro-organisms, as well as the rapid or gradual increase of salt concentration during acclimation. It has actually been shown that *Escherichia coli* exhibited the greatest degree of adaptability to NaCl in the early stationary growth phase (Doudoroff, 1940). Other major reports state that rapid shifts in salt concentrations have more adverse effects than gradual shifts (Lawton and Eggert, 1957; Kincannon and Gaudy, 1966; Hall and Smallwood, 1967; Kincannon and Gaudy, 1968; Burnett, 1974; Oren et al., 1992). Consequently, temporary reductions in BOD removal have already been observed, especially when the changes in salinity are combined with a high organic loading rate (Stewart et al., 1962). Another response to rapid changes in salinity is the release of cellular material, resulting in an increase of soluble COD (Kincannon and Gaudy, 1968). Although the adaptation of activated sludge has already proved to be possible, a major bottleneck is that the proper performance of such salt-adapted systems is usually limited to less than 5% salt (Hockenbury et al., 1978; Tokuz and Eckenfelder, 1978; Wong, 1992; Kargi and Dinçer, 1997; Dinçer and Kargi, 2001). Consequently the use of specialised organisms (i.e. halophiles) usually remains the best way to enhance the biological treatment of saline wastewater. This point will be emphasised in the next section. Finally, salt acclimation is quickly lost if salinity suddenly drops (Doudoroff, 1940; Kincannon and Gaudy, 1968), a scenario which is likely to happen since industrial effluents can be highly variable. In the leather industry for instance, the characteristics of the soak liquor are likely to change weekly or monthly, depending on every batch of hides and skins that is supplied to the tannery (Lefebvre et al., 2005).

3.2.2. Application of aerobic treatment to saline wastewater

It has been observed that high salinity can strongly inhibit the aerobic biological treatment of wastewater. However, in the 1940s, the follow-up of an activated sludge effluent treatment plant functioning with seawater showed that the efficiency of aerobic treatment was similar to that of a plant operating with fresh water (Pillai and Rajagopalan, 1948). The interest in the aerobic halophilic degradation of synthetic substrates has been increasing rapidly since the middle of the 1990s, as can be seen in Table 1. It can be seen from this table that the salinity of the effluents treated aerobically ranges from 10 to $150\,g\ l^{-1}$. In addition, most of the studies were based on synthetic wastewater that generally underwent treatment at a higher organic loading rate (OLR) and F:M ratio than industrial wastewater.

The contribution of Kargi and Dincer has been considerable, mainly using synthetic substrates (molasses). Kargi and Dinçer (1996a, b, 1997) were initially interested in the effect of salt concentration on the aerobic biological treatment of a synthetic saline effluent using a fedbatch biological reactor. The synthetic effluent was made up of diluted molasses, urea, KH_2PO_4 and NaCl up to a concentration of $50\,g\,l^{-1}$ and characterised by a COD:N:P ratio of 100:10:1. The treatment process used activated sludge. Kargi and Dincer (1997) observed that the effluent COD removal efficiency fell from 85% to 59% when salinity increased from 0 to 5%. Thereafter, Dinçer and Kargi (2001) tested innovative treatment processes in halophilic conditions including, for instance, a process with aerobic rotating discs whose number and surface area varied. This reactor was used to purify a synthetic effluent under conditions of increasing salinity (0–10%) and made it possible to exceed 80% of COD removal efficiency as long as the salt concentration remained lower than $50\,g\,l^{-1}$.

Table 1 also gives a few examples of attempts to adapt conventional micro-organisms to high salinity (Kargi and Dinçer, 1997; Uygur and Kargi, 2004). Yet, as already indicated above, use of halophilic inoculum is the best way to improve the performance of the aerobic treatment processes. For instance, the addition of a euryhaline *Halobacter* strain enabled Kargi and Dinçer (1996b) to significantly improve the performance of activated sludge. According to the same principle, *Halobacter halobium* was added thereafter to an activated sludge culture within an aerobic biofilter in which the cells were immobilised on ceramics particles (Kargi and Uygur, 1996). The continuous process was then operated at various salt concentrations. The addition of *Halobacter halobium* in the activated sludge led to improved performance of the reactor, in particular at the strongest salt concentrations. Finally, Kargi et al. (2000) were able to successfully treat an effluent generated by the pickling industry using activated sludge enriched in *Halobacter halobium*, exceeding 95% of COD removal. The same technique (inoculation of the halotolerant bacteria *Staphylococcus* sp. and *Bacillus cereus*) applied to another agro-industrial hypersaline effluent (15% of NaCl) generated by the production of plum pickles achieved COD removal efficiency of 90% in a sequencing batch reactor (Kubo et al., 2001). Another possible strategy consists in inoculating a mixture of halophilic organisms issued from diverse natural saline environments, such as salterns, in order to bring the organisms that will be able to stand high salt concentrations and treat the pollution at the same time. Such strategy has been employed, for instance, by Lefebvre et al. (2004, 2005) to treat various industrial saline wastewater (see Table 1). The

Table 1 – Aerobic treatment of high salinity wastewater

Substrate	Halophilic inoculum	Salt conc. ($g l^{-1}$)	Process	V (l)	COD in ($g l^{-1}$)	HRT (h)	OLR (kg COD $m^{-3} d^{-1}$)	MLVSS ($g l^{-1}$)	F:M ratio (kg COD kg^{-1} of MLVSS d^{-1})	COD remov (%)	Reference
Synthetic (molasse)	No	20	Fed-batch reactor	15	5	16	7.5	1.1	6.82	80	1
Synthetic (molasse)	No	50	Fed-batch reactor	15	5	13	9.3	1	9.23	59	1
Synthetic (molasse)	Yes	50	Rotating biodiscs	10	5	4	30	29	1.03	85	2
Synthetic (molasse)	Yes	100	Rotating biodiscs	10	5	4	30	28	1.07	60	2
Synthetic (phenol)	Yes	150	SBBR	1	0.29	24	0.29	3	0.10	99	3
Synthetic (phenol)	Yes	150	SBR	1	0.25	24	0.25	1	0.25	99.5	4
Synthetic (glucose. acetate)	No	60	SBR	5	1.2	6	4.8	—	—	32	5
Synthetic (≈SFPW)	Yes	32	Membrane bioreactor	8	5	36	3.4	11.2	0.30	85	6
Synthetic (≈SFPW)	Yes	32	Membrane bioreactor	3.6	1.2	13.7	2.1	11	0.19	91	6
Synthetic (≈SFPW)	Yes	10	SBR	10	0.55	20	0.7	4.1	0.17	87.9	7
Pickling wastewater	Yes	30–60	Activated sludge	Labo	4.6	35	3.2	4.9	0.64	96	8
Pickling wastewater	Yes	150	Activated sludge	5,000	120	168	17	—	—	60–70	9
SFPW	Yes	74	Fixed-bed	1.5	2.7	72	1	8	0.11	60	10
SFPW	Yes	20	Activated sludge	5	2.7	72	0.9	2.8	0.32	88	11
Tannery wastewater	Yes	35	SBR	10	3	120	0.6	2	0.30	95	12
Tannery wastewater	Yes	40	SBR	10	3.6	79	1.1	7.2	0.15	91	12
Tartaric industry effluent	Yes	120	SBR	5	4.3	240	0.4	3.5	0.12	83	13

Ref. 1. Kargi and Dinçer (1997); 2. Dinçer and Kargi (2001); 3. Woolard and Irvine (1994); 4. Woolard and Irvine (1995); 5. Uygur and Kargi (2004); 6. Dan et al. (2002); 7. Moon et al. (2003); 8. Kargi et al. (2000); 9. Kubo et al. (2001); 10. Gharsallah et al. (2002); 11. Khannous et al. (2003); 12. Lefebvre et al. (2005); 13. Lefebvre et al. (2004).

F:M ratio: food:microorganisms ratio; HRT: hydraulic retention time; MLVSS: mixed liquor volatile suspended solids; OLR: organic loading rate; SB(B)R: sequencing batch (biofilm) reactor; SFPW: seafood-processing wastewater; TDS: total dissolved solids; V: volume.

description, diversity and environmental characteristics of such sludge bacterial communities have been recently performed using molecular tools (Lefebvre et al., 2006a). The main conclusions were that halophilic sludge should be considered as possessing the same resources of diversity as conventional activated sludge and that such halophilic sludge biodiversity enables the biological treatment of hypersaline wastewater to be carried out with an efficiency similar to that observed in the treatment of fresh wastewater.

The sequencing batch reactor (SBR) is known to be particularly robust and to withstand extreme conditions. Consequently, it is not surprising that this process has often been employed to treat hypersaline wastewater. Woolard and Irvine (1994) were among the first to inoculate a sequencing batch biofilm reactor (SBBR) with moderately halophilic bacteria isolated from the Great Salt Lake, USA, in order to treat a synthetic effluent containing $150\,g\,l^{-1}$ of salt. The removal efficiency measured on phenol exceeded 99% with an influent phenol concentration of around $120\,mg\,l^{-1}$ and the pH not regulated. They renewed the experiment in 1995, with a free culture SBR, this time reaching a removal efficiency of 99.5% (Woolard and Irvine, 1995). More recently, Uygur and Kargi (2004) also used a SBR to cleanse a synthetic saline effluent. They observed a drop of COD removal efficiency from 90% to 32%, when salinity increased from 0% to 6%. Another study used a bench-scale SBR inoculated with halophilic sediments in order to treat an effluent from the tartar industry containing $120\,g\,salt\,l^{-1}$ (Lefebvre et al., 2004). The micro-organisms were able to treat carbon and nitrogen, provided the pH in the reactor was neutralised with phosphoric acid. Soluble COD and TKN removal attained 83% and 72% respectively. In another experiment, the aerobic treatment in a SBR of a saline tannery effluent ($34\,g\,NaCl\,l^{-1}$) achieved 95%, 93%, 96% and 92% removal of COD, PO_4^{3-}, TKN and SS, respectively, with a HRT of 5 days and an OLR of 0.6 kg $COD\,m^{-3}\,d^{-1}$ (Lefebvre et al., 2005). Finally, Ng et al. (2005) were able to treat synthetic wastewater in a SBR up to $60\,g\,l^{-1}$ of NaCl using acclimated biomass issued from domestic wastewater treatment plant. The dissolved organic carbon removal efficiency decreased from 96% to 86% when NaCl concentration increased from 0 to $60\,g\,l^{-1}$.

In addition to the effect of high salinity on organics removal, its impact on respiration rates is a well-known phenomenon. Early studies with *Bacillus cereus* indicated that the endogenous respiration rate of the culture decreased above 1% NaCl (Ingram, 1940). Kincannon and Gaudy (1966) found that relatively more oxygen was used by cells grown in the presence of high salt concentrations and they explained that NaCl may exert a selective pressure which fosters the predominance of species which have an inherently higher ratio of respiration to synthesis. Ludzack and Noran (1965) found similar results, as the initial respiratory activity of activated sludge after a chloride change increased. Yet, they also showed that sustained high chlorides generally depress respiration. Finally, recent studies utilising respirometric tests showed an inhibiting effect of high salinity on respiration rates of activated sludge (Pernetti and Di Palma, 2005). In batch-mode, a salt:biomass ratio of $30.7\,g\,salt\,g^{-1}$ of volatile suspended solids (VSS) induced a respiration inhibition of 84%, whereas in continuous-mode, a salt:biomass ratio of $35.5\,g\,salt\,g^{-1}$ of VSS gave a respiration inhibition of 81%. These experiments were conducted with activated sludge and the values of respiration inhibition could be well correlated to the loss in carbon removal efficiency.

There are other potential applications of hypersaline wastewater treatment. One instance is the recycling of a culture medium for microalgae (*Dunaliella salina*) producing beta-carotene, after biological treatment (Santos et al., 2001). In this experiment, this effluent rich in organic matter (glycerol) contained between 17% and 25% salt but the removal of glycerol proved possible provided that the sludge was supplemented with nitrogen, phosphorus, potassium and magnesium.

3.3. *Anaerobic digestion of saline effluents for the removal of organic matter*

3.3.1. *Effect of salt on anaerobic digestion*

The presence of high sodium and/or chloride concentrations has been traditionally considered as inhibitory for anaerobic wastewater treatment (Rinzema et al., 1988). It has been known for a long time that a sodium concentration exceeding $10\,g\,l^{-1}$ strongly inhibits methanogenesis (Kugelman and McCarty, 1965). However, Omil et al. (1995) could not show any clear toxic effect of a fish-processing effluent on an anaerobic pilot plant close to the anaerobic contact system. They showed that the adaptation of an active methanogenic biomass at the salinity level of the effluent was possible and they concluded that the efficiency of such a process depended on a suitable strategy for adapting the biomass to high salinity. Furthermore, Feijoo et al. (1995) stated that the toxicity of sodium in sludge depended on several factors, such as the type of methanogenic substrate used, the antagonistic effects of other ions at adequate concentrations, the nature and the progressive adaptation of sludge to high salinity. This last point appears to be of extreme importance, knowing that anaerobic digesters are usually more sensitive to high salinity than activated sludge units (Ludzack and Noran, 1965). However, as for aerobic sludge, continuous exposure of methanogenic sludge leads to the tolerance of a higher salinity than sludge exposed to salt shocks (Lema et al., 1988). Actually, in this experiment, a similar level of inhibition (i.e. 50% of methanogenic activity) was attained for continuous-exposure and for shock-exposure at a sodium content of higher than $20\,g\,l^{-1}$ and $6–13\,g\,l^{-1}$, respectively.

3.3.2. *Application of anaerobic treatment to saline wastewater*

The capability of halophilic organisms to biodegrade organic compounds by anaerobic digestion is well known. For instance, the anaerobic degradation of cellulose in a hypersaline lake and in a hypersaline lagoon has already been studied (Siman'kova and Zavarzin, 1992). However, anaerobic treatment assays of industrial saline effluents are rare; most of them are detailed in Table 2. It appears from this table that the anaerobic treatment has been tested on a certain number of saline effluents (mainly seafood-processing effluents) at salt concentrations ranging from 10 to $71\,g\,l^{-1}$, a range narrower than that in aerobic treatment.

Table 2 – Anaerobic treatment of high salinity wastewater

Substrate	Halophilic inoculum	Salt conc. ($g\,l^{-1}$)	Process	V (l)	COD in ($g\,l^{-1}$)	HRT (h)	OLR (kg COD $m^{-3}\,d^{-1}$)	MLVSS ($g\,l^{-1}$)	F:M ratio (kg COD kg^{-1} of MLVSS d^{-1})	COD remov (%)	Reference
Inuline effluent	No	10	UASB	1,100,000	7.9	6–8	23–32	18–31	0.7–1.8	65–80	1
Piggery manure	No	15	DFAFBR	1.4	1.9	96	0.5	—	—	90	2
Fish-farm wastewater	No	35	CSTR	15	70.1	660	2.5	25	0.10	55	3
Fishery effluent	Yes	40	CSTR	1.5	6	72	2	—	—	50	4
SFPW	No	15	UAF	1.1	34	288	2.8	57.1	0.05	83	5
SFPW	No	7.7–26.3	**UASB**	1	1.7	3	13.6	27.2	0.50	77	6
SFPW	No	13.6–33.7	Anaerobic contact system	150,00	10–60	180–240	1–8	—	—	70–90	7
SFPW	Yes	—	Hybrid USBF	2.3	1–1.5	18	1.5–2	7.4	0.2–0.3	70–90	8
SFPW	Yes	30	Anaerobic filter	2.5	5.5	9.2	14.3	—	—	70	9
Tannery wastewater	Yes	71	UASB	5	2.3	120	0.5	2.1–12.2	0.04–0.24	78	10

Ref. 1. Habets et al. (1997); 2. Rovirosa et al. (2004); 3. Gebauer (2004); 4. Aspé et al. (1997); 5. Guerrero et al. (1997); 6. Boardman et al. (1995); 7. Omil et al. (1995); 8. Mosquera-Corral et al. (2001); 9. Vidal et al. (1997); 10. Lefebvre et al. (2006b).

(AF: anaerobic filter; AFFR: anaerobic fixed film reactor; CSTR: completely stirred tank reactor; DFAFBR: down-flow anaerobic fixed bed reactor; F:M ratio: food microorganisms ratio; HRT: hydraulic retention time; MLVSS: mixed liquor volatile suspended solids; OLR; organic loading rate; SFPW: seafood-processing wastewater; TDS: total dissolved solids; UAF: upflow anaerobic filter; UASB: upflow anaerobic sludge blanket; USBF: upflow sludge bed-filter; V: volume).

The anaerobic digestion of seafood-processing wastewater has been widely studied for the past 10 years: a Chilean team focused in particular on the anaerobic digestion of fishery effluents, mainly those generated at the time of fish unloading. After recycling and primary treatment in order to eliminate proteins and grease, Aspé et al. (1997) showed that the effluent, containing 4–6 kg COD m^{-3}, 1.85 kg SO_4^{2-} m^{-3} and 16.2 kg Cl^- m^{-3}, could be treated anaerobically using a marine inoculum which induced specific methanogenic activity at 37 °C of 0.065 kg COD-CH_4 kg^{-1} of VSS d^{-1}. Aspé et al. (2001) also modelled the ammonia-induced inhibition phenomenon of anaerobic digestion and concluded that methanogenesis was the most inhibited stage. Later on, the treatment of seafood-processing wastewater was studied, using different processes, such as an anaerobic filter (Guerrero et al., 1997; Vidal et al., 1997; Mosquera-Corral et al., 2001), an upflow anaerobic sludge blanket (UASB) (Boardman et al., 1995) and an anaerobic contact system (Omil et al., 1995). The COD removal efficiencies obtained with this type of wastewater generally remained between 70% and 90%, with an OLR ranging from 1 to 15 kg COD m^{-3} d^{-1} and a SLR lower than 0.5 kg COD kg^{-1} of VSS d^{-1}.

Regarding the applications of anaerobic digestion to other saline effluents, the biological treatment assays have been rare. Rovirosa et al. (2004) were interested in the anaerobic digestion of a piggery effluent diluted in a saline synthetic water (15 g l^{-1} of salt), using a lab-scale down-flow anaerobic fixed-bed reactor (DFAFBR). The COD removal efficiency exceeded 90% for a hydraulic retention time (HRT) of 96 h and 68% for a HRT of 12 h. Finally, Lefebvre et al. (2006b) studied the anaerobic digestion of tannery soak liquor using UASB and reported that proper performance was limited to very low organic loads, which limited the applicability of such a process.

3.4. *Combined anaerobic/aerobic treatment of saline wastewater for nutrient (COD, N, P) removal*

Because both anaerobic and aerobic treatment of saline effluents have given only moderate performance on COD removal, the combination of these two modes of treatment has obviously been considered, with an aim to improve the performance of the overall treatment process. Panswad and Anan (1999) thus obtained COD removal efficiency close to 71% by applying an anaerobic/anoxic/aerobic process to a synthetic effluent containing 3% of salt, provided that the inoculum was first acclimatised to high salinity. More recently, Lefebvre et al. (2006b) treated a tannery wastewater and showed that the combination of UASB with an activated sludge post-treatment enhanced the performance of the overall wastewater treatment process and the COD removal efficiency of the combined anaerobic/aerobic treatment system reached 96%. Belkin et al. (1993) explained that a long anaerobic residence time actually contributes to the degradation of organic matter, to the reduction of toxicity and to the equalisation of influent variations. Hence, an anaerobic stage preceding the aerobic one permits to lower the load to which the aerobic stage is exposed afterwards, which enables lower aerobic installation and operating costs.

In addition to the removal of carbonaceous pollution, the combination of anaerobic/aerobic processes made it possible to address biological nitrogen and phosphorus removal from saline wastewater. Uygur and Kargi operated a SBR with alternating anaerobic, oxic, anoxic and oxic phases at various salt concentrations (0–6% of NaCl) in order to determine the NaCl-induced inhibition on the removal of nitrogen and phosphorus in a synthetic effluent (Uygur and Kargi, 2004). They observed that the removal efficiency of COD, N-NH_4 and P-PO_4^{3-} decreased when the NaCl concentration increased. The COD removal efficiency fell from 96% to 32% when salinity increased from 0% to 6% and, simultaneously, the removal of N-NH_4 and P-PO_4^{3-} decreased from 96% to 39% and from 84% to 22%, respectively. The addition of a *Halobacter* strain then made it possible to improve considerably the performance of the process, particularly at salinities higher than 2% (Kargi and Uygur, 2005). At a salinity of 5%, the COD, N-NH_4 and P-PO_4^{3-} removal efficiencies thus reached 73%, 51% and 31%, respectively, compared to 47%, 36% and 21% without the addition of *Halobacter*.

In particular, biological nitrogen removal at high salt concentrations through denitrification and nitrification has been addressed by a large number of studies:

3.4.1. *Denitrification*

The capacity of halophiles to use oxyanions as final electron acceptors is a well-known phenomenon. In the middle of the 1980s, extremely halophilic bacteria had already been isolated from various sites and cultivated anaerobically in the presence of nitrate (Hochstein and Tomlinson, 1985). Many of these isolates were able to produce nitrite, nitrous oxide and nitrogen gas. These results confirmed the existence of extremely halophilic denitrifying bacteria and their presence within a large variety of hypersaline environments. However, the application of these properties to the treatment of nitrogen encountered difficulties: Dinçer and Kargi (1999) showed that salt concentrations higher than 2% were responsible for significant reductions in the nitrification and denitrification performance of biological reactors and that denitrification was affected by salt more than nitrification. Dincer and Kargi thus contradict Panswad and Anan (1999), who showed that denitrifying bacteria could tolerate high salinities better than nitrifying bacteria, the latter being more tolerant than the heterotrophic bacteria responsible for carbonaceous pollution removal. Panswad and Anan were thus able to acclimatise a denitrifying community to saline conditions and maintain a nitrate reduction rate of 2 mg N-NO_3^- g SS^{-1} h^{-1} at 30 g NaCl l^{-1}.

3.4.2. *Nitrification*

The salt-induced inhibition of nitrifying bacteria is a well-known phenomenon (Ludzack and Noran, 1965). But these results have only recently been refined by multiple studies. Chen and Wong (2004) showed that the progressive adaptation of a continuous nitrifying activated sludge culture to chlorides gave better results than those of another culture operated at fixed chloride concentrations. However, beyond 18.2 g Cl l^{-1}, nitrification became unstable. Thus, they support the conclusions of Dahl et al. (1997) who showed that nitrification could take place under operational conditions up to 20 g $Cl\,l^{-1}$, with a maximum nitrification rate of 2 mg N g $VSS^{-1}\,h^{-1}$. In addition, Dahl et al. showed that a rapid increase in the chloride concentration had an inhibiting action on the nitrifying bacteria. Thereafter, Campos et al. (2002) showed a combined salt- and ammonia-induced inhibition of nitrification: the accumulation of ammonia started at an ammonia loading rate of 3 g N-$NH_3\,l^{-1}\,d^{-1}$ and a salt concentration of 525 mM (13.7 g $NaCl\,l^{-1}$, 19.9 g $NaNO_3\,l^{-1}$ and 8.3 g $Na_2SO_4\,l^{-1}$). This supports the view of Vredenbregt et al. (1997), who showed that in a fluidised bed, nitrification was possible up to 34 g $Cl\,l^{-1}$ on the condition that the ammonia load was maintained at 15 mg $NH_3\,l^{-1}\,h^{-1}$. Lastly, Panswad and Anan (1999) observed only a moderate reduction in the nitrifying activity from 4 to 3 mg N-NH_3 oxidised g^{-1} of SS h^{-1} after NaCl concentration increased from 5 to 30 g l^{-1}, provided that the sludge was acclimated to high NaCl concentrations. In addition, the recovery capacities of nitrifying bacteria following a shock of 70 g l^{-1} of NaCl proved to be excellent.

4. Effect of high salinity on turbidity and sludge properties

Decantation problems in saline environments have frequently been reported in the literature and multiple reasons have been given for this phenomenon (Woolard and Irvine, 1995). First, the density of salt water is higher than that of freshwater, thus creating greater resistance to decantation through higher buoyant forces. Second, high salt concentrations cause cell plasmolysis and death of micro-organisms usually present in sewage due to the increase of osmotic pressure, which results in a reduction in particle size and density (Kargi and Dinçer, 1997). Third, hypersalinity is also known to reduce the quantity of the filamentous bacteria that play a part in the mechanical integrity and structure of the flocs. Finally, the lack of protozoans can also influence effluent turbidity. Protozoans, indeed, reduce the turbidity of the effluents by grazing the micro-organisms, but it has been shown that their resistance to salinity shocks is limited and they do not normally survive more than 24 h after a NaCl shock higher than 40 g l^{-1} (Salvado et al., 2001). This explains why protozoan scarcity is expected in saline environments and has been stated for instance by Ng et al. (2005) who observed the disappearing of ciliates from activated sludge above 10 g l^{-1} of NaCl. However, the observations of Pillai and Rajagopalan (1948) showed that under stable conditions seawater is not an obstacle to the development of ciliates and that the performance of an effluent treatment plant operating with seawater was dependent on the number of these protozoans.

Membrane bioreactors could provide an adequate solution to the sedimentation problems encountered at high salt concentrations. They have actually seldom been applied to saline wastewater treatment even though they have been used to prevent the wash-out of a pure culture of a halotolerant sulphate-reducing bacterium, *Desulfobacter halotolerans*, in the treatment of saline sulphate-rich wastewater (Vallero et al., 2005). Finally, one study, appearing in Table 1, compared the performance of a yeast membrane bioreactor (YMBR) to that of a bacterial membrane bioreactor (BMBR) (Dan et al., 2002). The maximum COD removal reached 0.93 g COD g^{-1} SS d^{-1} for the YMBR with a F:M ratio of 1.5; and 0.32 g COD g^{-1} SS d^{-1} for the BMBR with a F:M ratio of 0.4. The clear conclusion was that BMBR could be recommended for small F:M ratios, while YMBR became more competitive when this ratio increased. In addition, they noticed that the silting up of membranes was more limited in the case of YMBR.

In spite of the negative effects of salt on effluent turbidity, it seems that it is not an obstacle to microbial growth. Panswad and Anan (1999) did not observe any effect of high salinity (30 g $NaCl\,l^{-1}$) on the suspended solids concentration in a bioreactor, provided that sludge was previously acclimated. Kubo et al. (2001) also obtained a suitable biomass growth at a salinity of 15%. In addition, settling properties can be good even at high salt content, although it was shown that increasing salt content induced higher sludge volume indexes (SVI) (Kargi and Uygur, 2005). Among the first, Kincannon and Gaudy (1966) noticed that in some reactors acclimated to high salt concentrations, sludge consisted in dispersed systems practically devoid of any flocculating tendency, whereas in some other reactors, the sludge did flocculate. In any case, the biochemical response of the sludge was the same. Panswad and Anan (1999) did not observe any effect of high salinity on sludge settling and the studies of Campos et al. (2002) confirmed these results and showed that high salinity does not have a long-term effect on the sludge physical properties. They were able to maintain a concentration of 20 g $VSS\,l^{-1}$ in an activated sludge reactor thanks to a SVI of 11 ml gVSS^{-1}. Kargi and Uygur also showed that SVI depended on sludge age and was minimum (55 ml gVSS^{-1}) at a sludge age of 10 days in a sequencing batch reactor (Kargi and Uygur, 2002). In addition they showed that SVI decreased with increasing OLR resulting in minimum SVI of 46 ml gVSS^{-1} at a OLR of nearly 86 mg COD h^{-1} (Kargi and Uygur, 2003). Finally, Uygur and Kargi (2004) found that SVI increased with salinity, but the SVI value (97 ml g^{-1}) that was achieved at a salt content of 6% in a SBR showed the good settling properties of the sludge, even at high salinities. Moon et al. (2003) explained that the settling properties of the sludge were related to size and fractal dimension of flocs. Finally, Ng et al. (2005) explained that SVI and turbidity are not necessarily related directly because they reflect different physical issues: the SVI reflects the compactability of the biomass whereas turbidity reflects the ability of dispersed organisms to flocculate.

5. Global hypersaline wastewater treatment chain for the removal of salt and organic matter

It appears from the points treated previously that several physico-chemical and biological techniques can be applied to the treatment of wastewater containing high salinity. All these techniques present advantages and disadvantages. According to the results obtained with various treatment systems, it appears clearly that the optimal treatment system for saline wastewater involves a combination of several techniques. Fig. 1 indicates the generic sequence of the different operations that can be indicated for the treatment of industrial saline wastewater.

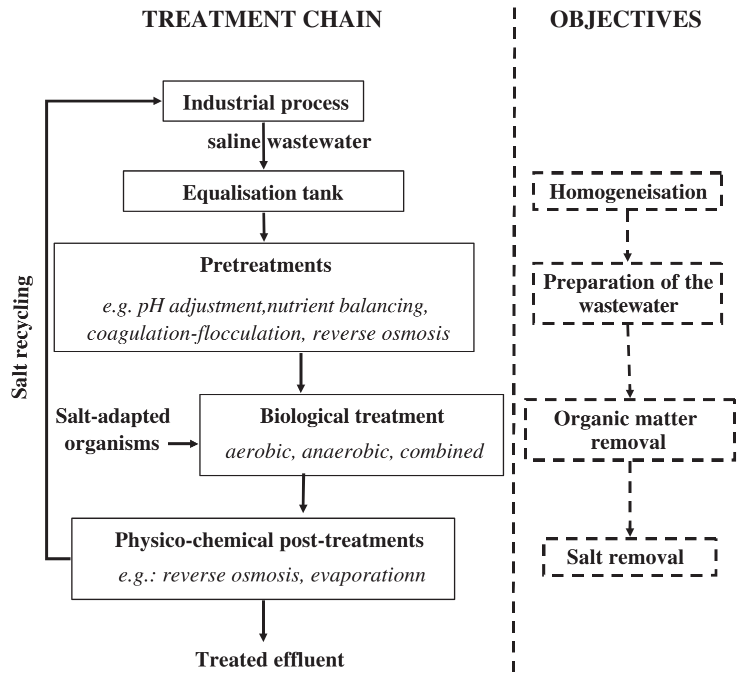

Fig. 1 – Simplified generic sequence of the global treatment chain of hypersaline wastewater.

Firstly, the construction of an equalisation tank appears to be of extreme importance in order to avoid organic and salt shocks to biological treatment systems. Other pretreatments include pH adjustment, nutrient balancing, as well as coagulation–flocculation for the removal of colloids, and, eventually, RO for salt removal. Yet, as already stated above, pretreatments such as UF are often required for efficient operation of a RO unit in order to eliminate foulants from the feed wastewater. However, UF-pretreated feed water may still contain dissolved organic compounds that will contribute to RO membrane fouling (Winters, 1997). Hence, in most cases, RO should take place as a post-treatment, after primary and biological treatment for the removal of colloidal as well as dissolved organic matter.

Following pretreatments, biological treatment using properly adapted biomass could achieve carbon, nitrogen and phosphorus removal. Physico-chemical post-treatments should then consist in the removal of salts, which can be achieved efficiently by reverse osmosis. Finally, the concentrate residue separated by RO should be evaporated and then, if its purity is adequate, recycled at the head of the process.

6. Conclusion

In this review it has been shown that the treatment of saline wastewater is feasible, though the obstacles created by high salt concentrations are considerable. The use of RO is particularly efficient for the removal of salts, yet the high amounts of suspended solids and organic matter in effluents reduce the life time and the efficiency of the membranes involved. Consequently, the optimal treatment of highly saline wastewater should usually involve a biological treatment prior to salt removal. Biological treatment is inhibited by high salt concentrations. However, it has proved feasible to use salt-adapted micro-organisms capable of withstanding high salinities and at the same time of degrading the pollutants that are contained in wastewater. The selection of salt-tolerant micro-organisms involves an adaptation of the sludge to high salt concentrations. Furthermore, the effluent organic loading rate and salt concentration should be equalised as far as possible, as these micro-organisms are sensitive to environmental shocks, especially in anaerobiosis. Nevertheless, after proper adaptation, many salt-tolerant strains have proved capable of removing efficiently the organic matter from saline effluents, including nitrogen and phosphorus. The use of these micro-organisms is therefore recommended in the treatment of saline effluents, prior to salt removal by physico-chemical treatment.

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