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Ammonia retention capacity of nanofiltration and reverse osmosis membranes in a non steady state system, to be use in recirculation aquaculture systems (RAS)

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ABSTRACT

Recirculation aquaculture systems (RAS) need to control ammonia level because the high toxicity on fish. For this, nanofiltration membrane has been proposed in the first part of our study to separate ammonia from water. We discussed different membranes as well as transmembrane pressure (TMP) and pH to achieve the best results for ammonia retention (AR). In this second part we analyze the influence of the ammonia concentration on AR to obtain higher concentrated volume that can be separated of the system and treated later. A model solution in a non-steady state was used, where the ammonia concentration increase over the time. Since water has similar molecular weight that ammonium ions, the mechanisms for the rejection of ammonia are based on the repulsive electrochemical forces on the active layer. A RO membrane DSS-HR98PP and three NF membranes, NF90, NF200 and NF270 were tested over a range of 0–11.45 mg/L under optimal TMP of 16 bar for NF membranes and 24.5 bar for the RO membrane. Projecting the results to the RAS, NF270 is the most efficient for ammonia retention, as both flux and AR influence the engineering design concept. For example, treating 2000 L/h with an ammonia concentration of 7 mg/L, removal is 17.5 g/m^2 day with a membrane area of 13 m^2 and TMP of 16 bar.

1. Introduction

In the first stage of this study (Cancino Madariaga et al., 2011) we analyzed the effects of pressure and pH on three nanofiltration (NF) membranes, NF 200, NF 270 and NF 90, and on DSS-HR 98PP, a reverse osmosis (RO) membrane. The range used was based on the aquaculture pH level, i.e. between 5 and 7, and an ammonia concentration in terms of NH_4^+. Transmembrane pressure (TMP) is the force that pushes the liquid through the membrane, resulting in retention of part of the ammonia by the membrane, with the other fraction passing through the membrane. However, additional effects on ammonia retention (AR) were discussed, finding that molecules with similar molecular weight to that of water (18 g/gmol) and NH_4^+ (17 g/gmol) have different retention rates due to the ionic force and the Donnan effect.

In this paper the effects of the ammonia concentration on AR are explained. It may be expected that NH_4^+ concentration will have a negative influence on AR, where higher concentration produces lower AR; however, there is no clear evidence and the results depend on the membrane used. For recirculation aquaculture systems (RAS) this behaviour becomes interesting, as the ammonia concentration increases over the time and the concentration limit for use with membrane processes must be identified before any investment in the new technologies and applications can be made. Thus, the aim of this paper was to analyze the capacity to retain ammonia by NF and RO membranes in a non steady state system, where the concentration of ammonia is increasing during the time, at pH and concentration conditions interesting for aquaculture applications.

1.1. Controlling ammonia compounds in aquaculture

Traditional processes to control ammonia compounds in recirculation aquaculture systems (RAS) use nitrifying bacteria.

Nitrification is produced by two different species of bacteria in two consecutives stages, *Nitrosomonas* to convert ammonia (NH_4^+ or NH_3) to nitrite (NO_2^-), and *Nitrobacter* to convert nitrite to nitrate (NO_3^-) (Chen et al., 2006; Emparanza, 2009).

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Table 1
Percentage of un-ionized ammonia at different temperatures and pH for zero salinity in aqueous ammonia solution.

Temperature (°C)	pH					
	6.0	6.5	7.0	7.5	8.0	9.0
5	0.013	0.04	0.125	0.394	1.24	11.1
10	0.019	0.059	0.186	0.586	1.83	15.7
15	0.027	0.087	0.273	0.858	2.66	21.5
20	0.04	0.125	0.396	1.24	3.82	28.4
25	0.057	0.180	0.566	1.77	5.38	36.3
30	0.081	0.254	0.799	2.48	7.45	44.6

Source: Adapted from US EPA (1979).

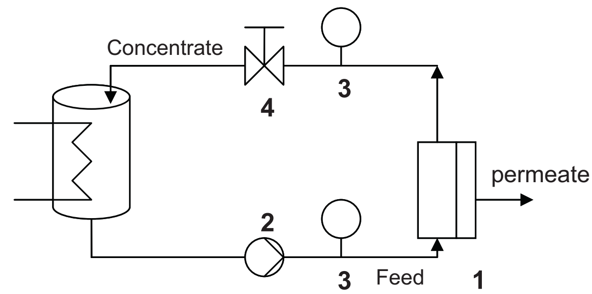

Fig. 1. Partial recirculation system under non steady-state conditions. (1) Flat high pressure cell, (2) high pressure pump, (3) manometers and (4) valve.

However, the efficiency of the nitrification process presents a high degree of fluctuation, as the bacteria are influenced by environmental disturbance and changes in operating conditions (Malone and Pfeiffer, 2006; Graham et al., 2007). This situation arises because fish farmers must constantly change their fish culture strategies according to the biomass or the number of fish present in the RAS. Normally, the RAS system is designed according to the maximum possible level of biomass the system can produce, and this design is made prior to the installation. The problem appears when the fish culture produces lower biomass than was originally planned, which is a strategy used by fish farmers when prices are low or because other options or species are being introduced. This change in the level of biomass present in the RAS means the quantity and quality of water also changes, and although the system can be adapted to some degree of change, it is not possible to affect changes as fast as is necessary. This perturbance means additional stress on the bacteria because the substrate is not constant, and this therefore affects the efficiency of the biofilter. A dynamic system like membrane process would clearly be better in these circumstances, in which it was possible to adapt the system rapidly in accordance with the level of biomass in culture.

Stress also affects the species in culture, since total ammonia nitrogen (TAN) compounds cannot be maintained at an adequate level (Svobodova et al., 2005).

High levels of nitrite have toxic effects (Malone and Pfeiffer, 2006; Cheng et al., 2004), due to increased alteration or chronic diseases (Emparanza, 2009). Ammonia concentrations between 30 and 300 μg N/L produce mortality in salmon and with lower concentrations of around 10 μg N/L disease can arise in gills (Liltved et al., 2009). Cheng et al. (2004) mention a level of 12.5 μg N/L as an acceptable level of NH_3 (un-ionized ammonia) as it is more toxic than NH_4^+ (ammonium ion). According to US EPA (1995) in aquatic life the toxicity of un-ionized ammonia is approximately 100 times greater than ionized ammonia.

According to Liltved et al. (2009), there is no clear answer to TAN limits; however other authors give some ranges that can be considered as acceptable in cultures. The ranges of TAN limits depend on pH and temperature as the equilibrium between NH_3 and NH_4^+ in water depends on these parameters, and as was mentioned above, their toxicity is different. For example, for 1 mg N/L TAN at 15 °C and pH 7, i.e. under standard conditions (US EPA, 1995), only 0.273% corresponds to NH_3, i.e. 0.00273 mg/L NH_3 (see Table 1), which is an acceptable value for salmon, a species that is sensitive to ammonia (see Table 2). The remainder of the 1 mg N/L corresponds to NH_4^+. In a more extreme case, with a TAN of 10 mg N/L, the un-ionized ammonia under the same conditions of pH and temperature will be 0.0273 mg/L, which is also acceptable for salmon.

The ammonia criteria according to US EPA (2009), establish an acute concentration "of 2.9 or 5.0 mg N/L (at pH 8 and 25 °C) depending on whether freshwater mussels are present or absent, and a chronic criterion of either 0.26 or 1.8 mg N/L depending on the same". For fish, the acute criterion depends on pH alone and the chronic criterion on pH and temperature (US EPA, 1999). Also the limits for the tolerance or susceptibility to ammonium compounds depends of the size of the fish (US EPA, 2009; Zhang et al., 2012; Biswas et al., 2006) has produced an extensive list of TAN limits for different species of mussels and fish with a wide reference list.

As a result of all these effects on RAS production, the elimination or separation of ammonium compounds is an important issue to be resolved. Others factors also lead to the same necessity, such as current environmental law and regulations (Hung et al., 2003; Hasanoğlu et al., 2010; Mirzoyan et al., 2008), which are increasingly strict for RAS. In this scenario, new technologies, such as membrane process represent an important opportunity for development and study.

2. Materials and methods

All experiments were carried out in a continuous and non-recirculation mode (Fig. 1), i.e. under non steady-state conditions, using a flat stainless steel high pressure cell, as described in Cancino Madariaga et al. (2011). The high pressure cell was developed and designed by the GKSS Research Centre (Geesthacht, Germany) and included some modifications done at the Laboratories of the Inpromem (Chile). To drive the flow, a high pressure Speck GmbH pump (Germany) working between 0 and 140 bar was included, and to control temperature a Chiller, RESUN, model C-1500 was used (Cancino Madariaga et al., 2011). In the non recirculation mode, the permeate flow is discharged of the system and the concentration increase through the time, i.e. the membrane is used to concentrate the ammonia. The ammonia concentration is determinated in the initial solution and in the permeate through the time to observe if the ammonia go through the membrane. The idea is to concentrate the ammonia, obtaining a free ammonia permeate.

Ammonia concentration was measured using a multiparameter photometer Hanna Instruments model HI-83000 (resolution of 0.01 mg/L and deviation of ±0.02), used with an special kit and the tungsten lamp at 420 nm based on Nessler method. All the analyze were made in triplicate and the results were processed statistically using the commercial software centurion Statgraphics Centurion XVI (StatPoint, USA, 2010).

Four commercial membranes were used: NF 90, NF 200 and NF 270 from Dow Liquid Separations, USA and DSHR98PP provided by Alfa Laval, Denmark. Membrane characteristics, membrane pre-treatment and working conditions were described in Cancino Madariaga et al. (2011). The main characteristics of the membranes are showed in Table 2.

The initial ammonia model solution was prepared using distilled water with a conductivity lower than 5 μS/cm and ammonium salt ($NH_4^+Cl^-$, Merck Germany). Because the pH and temperature conditions studied, all the ammonia was in the ionized ammonia form (NH_4^+). Ammonia concentration were ranged between 0.8 and 11.45 mg/L for the membranes in the feeding tank. The experiences