



Heavy metals removal from influents to prevent mortality in salmon fry



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ABSTRACT

The concentration of heavy metals in water, above certain values, threaten industrial salmon production and have occurred in two of the most important salmon producers, Norway and Chile. Aluminum and iron are two of the main heavy metals found in fresh water of the salmon industry, although manganese, zinc and copper have also been detected. In Chile, an experimental study found a solution to remove aluminum, iron and manganese. The present works studies copper and zinc removal by ionic exchange using AMBERLITE IRC747. The resin's removal capacity is 0.025 meq/g and does not depend on the solution's pH. An ionic exchange column was designed and continuously operated to remove copper and zinc from concentrations equal to 1000 µg/L of each metal. Then, the column was modularly operated with an aluminum, iron and manganese abatement system removing them by precipitation, oxidation (for iron and manganese) and granular filtration. When operating the modular system, the final aluminum, copper, iron, manganese, and zinc concentrations were 0.1, 0.4, 0.6, 0.8 and 0.3 µg/L, respectively. As a result, the system implemented obtained values below the maximum limits allowed for aluminum, iron, manganese, copper and zinc.

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1. Introduction

In Chile, there have been events of acute fish mortality due to the presence of heavy metals (Kristensen et al., 2009). Salmon fry have suffered toxicity as well as irritation, hemorrhaging and necrosis in the branchias, an effect that can be more or less aggravated depending on the water's hardness or alkalinity (Pandey et al., 2008).

It has been shown that some metals (such as copper and zinc) decrease survival, fertility and hatchability (Iwasaki et al., 2010). Highest mortalities founded in water reuse aquaculture systems (RAS) had been related with highest copper levels (0.056 mg/L) in those systems (Davidson et al., 2009); also it had been reported that survival time is inversely proportional to concentration of zinc (Skidmore, 1964).

Aluminum, iron and manganese have been satisfactorily removed, achieving concentrations compatibles with salmon farming, using a two-stage process in series that considers precipitation due to changes in pH and granular filtration. The first stage removes aluminum and the second one removes iron and manganese (Aspe et al., 2012). In contrast, there are no reports in the literature on Cu and Zn removal in the industrial salmon context. For these reason, in this case, it is necessary to remove

these metals from the influent water to achieve in the culture metal concentrations less than sub-lethal and lethal concentrations.

Heavy metals concentrations threshold that cause sub-lethal or lethal toxic effects are dependent on other chemical variables present, such as pH, hardness and salinity. Table 1 shows the limits toxic for copper and zinc in function of the hardness.

One of the alternatives most used to remove copper and zinc is ionic exchange. This method is a promising alternative to diminish the concentration of these metals since ionic exchange resins possess a high capacity to remove ions at low concentrations, are stable and easily regenerated (Lin and Juang, 2005). Thus, the objective of the present paper is to study the incorporation of a third stage to remove copper and zinc from water using an ionic exchange column, which at the same time can be added to the already existing metal abatement system used to remove Al, Fe and Mn. For the design of this column, the removal capacity of resin must be determined for pure and mixed solutions. It has been demonstrated in cationic resins that the capacity is a function of pH (Lin and Juang, 2005). Consequently, the resin's removal capacity and the optimal pH must also be determined.

2. Materials and methods

The cationic resin AMBERLITE IRC747 (see Table 2) was used because it has high affinity for copper and zinc. Its regeneration

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Table 1
Total maximum concentrations zinc (mg/L Zn) and copper (mg/L Cu) in different water hardness (mg/L CaCO₃) for salmonid waters.

| Water hardness (mg/L CaCO ₃) → | 10 | 50 | 100 | 300 | 500 |
|--|-------|-------|------|-------|-----|
| Dissolved zinc concentrations (mg/L Zn) | 0.03 | 0.2 | 0.3 | – | 0.5 |
| Dissolved copper concentrations (mg/L Cu) | 0.005 | 0.022 | 0.04 | 0.112 | – |

Source: European Parliament (2006).

Table 2
Properties of Amberlite IRC747.

| Functional group | –CH ₂ –NH–CH ₂ –PO ₃ Na ₂ |
|-------------------------------|---|
| Exchange total capacity | ≥1.75 equiv./L (Na ⁺) |
| Operation maximum temperature | 80 °C |
| Minimum height of the bed | 700 mm |
| Operation pH | Without restriction |
| Minimum copper removal pH | 2.0 |
| Minimum copper removal pH pH | 2.5 |
| Chemical reaction | R–CH ₂ –NH–CH ₂ –PO ₃ Na ₂ + M ²⁺ → R–CH ₂ –NH–CH ₂ –PO ₃ M + 2Na ⁺ |
| Regeneration | HCl (1 N) |
| Na ⁺ conversion | NaOH (1 N) |

Source: Haas (2010).

requires 2 mL of HCl 1 M and 2 mL of NaOH 1 M for each gram of dry resin.

The metals were analyzed (APHA-AWWA-WPCF, 1992) used to measured metals concentrations was the atomic absorption spectroscopy (method 3500) and the equipment used was an atomic absorption spectrophotometer (Perkin-Elmer, 1100-B, USA). The detection limit of the atomic absorption spectrophotometer is 0.01 µg/L (Kastenmayer, 2008).

2.1. Batch assays

To determine the resin's capacity, three batch assays were performed: copper and zinc removed separately and then with both metals in the solution. All the assays were performed in the following conditions: volume (800 mL), initial concentration (1000 µg/L of the ion or ions present), quantity of resin (2 g) and 1 h of reaction time. To determine the resin time-out, solution conductivity during the reaction was measured, using a cell immersion (Cole-Parmer H-01481-64) and a digital conductivity meter (Cole-Parmer H-19101-00) until it is retained constant in time. In addition, to

study the initial pH effect, four batch assays (each one, in triplicate) at different initial pH (between 5.8 and 9.8) with all other experimental conditions constant were carried out. The resin capacity was determined according to the following equation:

$$A = V[(C_{i,Zn} - C_{f,Zn})e_{Zn}] + A = V[(C_{i,Cu} - C_{f,Cu})e_{Cu}]$$

where A is capacity resin, in equiv./g, V is the solution volume, in L, $C_{i,x}$ is ion initial concentration "x" (x: copper or zinc) in mg/L, $C_{f,x}$ is the ion "x" final concentration in mg/L and e_x are "x" ion equivalent in equiv./mol.

2.2. Continuous operation at the ionic exchange column

An acrylic column 60 mm in diameter and 108 cm high contained 0.89 kg (1.9 L) of resin, considering both the resin's capacity and pH of the operation. The assays were continuous and performed with a flow of 0.3 L/min for 6–7 h. Previously, it was determined that over 7 h of operation resin depletion occurred.

Three preliminary assays in the ionic exchange column were performed to remove copper and zinc; two in order to identify the optimal location of the feed (top or bottom) at feed concentration of 1 g Cu/L, and 1 g Zn/L. The assay third was fed with 10, 100, 10, 1000 and 1000 µg/L of Al, Fe, Mn, Cu and Zn, respectively. The Al, Fe and Mn concentrations corresponds to the maximum allowed for salmon (Aspe et al., 2012).

2.3. Modular system operation

The modular system (to see Fig. 1) was built by placing the existing system to remove Al, Fe and Mn in series with the ionic exchange column which was operated at 19 °C and the input and output pH of the ionic exchange column were 7.1 and 8.8, respectively (without pH control).

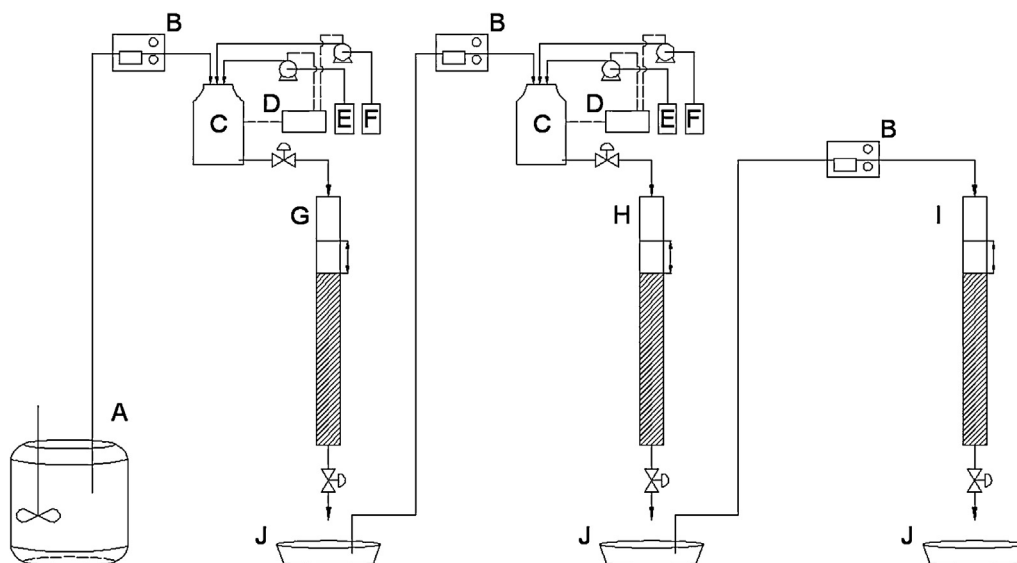


Fig. 1. Modular system scheme. A: Metal solution container, B: Peristaltic pump, C: Vessel to control pH, D: pH controller; E: HCl 0.4 M container, F: NaOH 0.1 M; container, G: Column 1, H: Column 2, I: Column 3, J: Column discharge vessel, L: over the fill liquid level.

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