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Long-run operation of a reverse electrodialysis system fed with wastewater solutions

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In the framework of salinity gradient power technologies, reverse electrodialysis (RED) is one of the most promising. In RED, two solutions of different salt concentration are fed into a series of alternate compartments, the one fed by the low salinity solution, the other by the high salinity solution. Compartments are separated by anion and cation exchange membranes alternatively piled to form a stack. Selective ion transport from the concentrate compartment to the dilute one across the membranes allows to generate an ionic current, which is eventually converted into electric current by means of suitable electrode compartments closing the stack.

Several options for the feed solutions are possible. Natural waters were first considered as a potential source of salinity gradient, such as: river water and seawater or concentrated brines and low-salinity waters. Another alternative is the use of artificial solutions as feed solutions within closed-loop systems in which deployed salinity gradient of solutions exiting the RED unit is then regenerated by means of a regeneration step (e.g.: using low-grade heat, in RED heat engines; or , using electricity, in RED batteries).

A nascent, still less explored alternative is the use of different industrial wastewaters as feed solutions. In fact, in several different scenarios, waste streams to be disposed can actually represent a very effective source of salinity gradient to be exploited before the natural mixing with the receiving water body occurs.

In the present work a high salinity waste brine from a fish processing factory and a low-salinity water from a civil wastewater Membrane Bio Reactor (MBR) treatment plant were selected as feed solutions for an extensive investigation on a laboratory-scale RED unit (10 cell-pairs with a 10 cm × 10 cm active membrane area). Firstly, the RED unit performance was characterized with artificial NaCl solutions prepared with the same NaCl concentration as the real streams, in order to have a comparison-reference for tests with real solutions. Subsequently, long-run tests with real feed solutions were performed (firstly feeding real brine and artificial low-salinity feed, then artificial brine and real low-salinity feed and, finally, feeding the stack with both real feed), operating the RED unit in an uninterrupted way for more than 2 weeks for each case. The time-evolution of system performance parameters (pressure drops, stack resistance, power output, etc.) was registered and analyzed in order to assess the relevant effect of the real feed solutions, likely related to fouling/scaling/plugging phenomena in the lab-stack. Also counter washing and chemical washing procedures were periodically (typically, once per week) implemented in order to highlight their effectiveness in restoring process performance. On overall, results collected over a period

of more than 2 months, represent an original and unique source of information on the long-time performance of RED systems with such unconventional real feed solutions.

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Experimental investigation on the efficiency of zinc(II) recovery from waste streams by TBP liquid-liquid extraction

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In many industrial processes the presence of zinc in the wastewater may represent an obstacle to its high efficient regeneration. This is the case of the treatment of spent pickling solutions aiming the recovery of hydrochloric acid via pyrohydrolysis techniques. Hydrochloric spent pickling solutions from steel processing contain relevant amount of metals such as iron (Fe) and zinc (Zn) that may significantly affect recovery of hydrochloric acid (HCl) through pyrohydrolysis. In fact, although Fe can be recovered as ferric oxide (Fe_2O_3), being the main solid product of the pyrohydrolysis process, zinc chloride (ZnCl2) evaporating can occlude nozzles and stick to the pyrohydrolysis reactor walls, thereby contaminating the iron oxide product. Thus, efficient removal Zn is needed. Of note, Zn recovery is economically affordable and can provide commercially valuable by-products such as zinc chloride or sulfate.

In this study, we present the results obtained within a laboratory experimental campaign to recover Zn and Fe from pickling liquors by means of liquid-liquid extraction adopting a suitable organic extractant, tributyl phosphate (TBP). In order to find out the best operative conditions leading to very high efficiencies, three main factors were investigated: the volume ratio between the organic extractant and the aqueous spent pickling liquor, the stirring time, and the percentage of TBP used (pure or variously diluted in kerosene). Furthermore, a parallel study was carried out for the analysis the efficiency of the stripping step, performed with the aim of regenerating TBP and recovering Zn and Fe by suitable aqueous stripping solutions. The results in terms of recovery yield and selectivity of Zn recovery over Fe ions were obtained and analyzed.

Keywords: Spent pickling liquor; Zinc(II) removal; Liquid-liquid extraction.

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