TREATMENT OF WASTE WATER FROM CALCIUM NITRATE PRODUCTION BY ELECTRODIALYSIS

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Abstract

A process for cleaning of waste water from calcium nitrate (CN) production is described in this study. Electrodialysis (ED) was used in the process. A pilot ED module was tested with real waste water containing CN. Tests were carried out both in batch and in feed&bleed mode. Concentration at the beginning of the batch test was 20 g/L of CN and a dependence of salt removal on concentration was obtained from results. Concentration of the treated solution in feed&bleed was in the range 0.8 – 80 g/L of CN and it demonstrated to achieve concentrate stream with concentration higher than 240 g/L of CN. All results from the pilot tests were useful for a design of an industrial ED technology in capacity of 200 m^3/d.

Key words: *electrodialysis, calcium nitrate, waste water, fertilizer*

1. INTRODUCTION

Calcium nitrate (CN) belongs to important fertilizers and it is produced by a reaction between nitric acid and calcium carbonate. Waste water with a high content of nitrates is produced during the operation. The concentration is too high for direct discharge into rivers and too low for reuse in the production plant. There are several ways to treat waste water in fertilizer industry: evaporation (CEAMAG 2014), ion exchange (Kumpović & Leaković 2011) and a membrane separation process such as reverse osmosis (Eriksson 2004, Noworoty, Koziol & Trusek-Holovnia 2003).

This paper presents the experience of waste water treatment from CN production by an electrodialysis process.

Electrodialysis (ED) belongs to electromembrane processes which are able to remove electrolytes. ED found a wide spectrum of applications in e.g. desalination of brackish water, production of edible salt from seawater, desalination of cheese whey, potassium tartrate removal from wine, recovery of salts of organic acids from fermentation broth (Davis, Grebenyuk & Grebenyuk 2001) An electrodialysis module is the core of all ED technologies. The ED module consists of two electrodes, an alternating order of cation exchange membranes (CM) and anion exchange membranes (AM), working and electrode spacers. The electrodes generate an electric field which drives the ionic transport inside the module. Only cations can pass through the CM and only anions can pass through the AM. The feed solution flows inside working spacers and ions migrate through the membranes (Fig. 1). In this way, two main streams are generated: diluate, a solution with lower salt content than the feed, and concentrate, a solution with higher salt content than the feed. The electrode spacers are the closest to the electrodes and comprise the electrode chambers. In these chambers electrode reactions take place and the electrode gases are produced (Strathmann 2010).

2. EXPERIMENTAL

The first set of experiments was carried out in a batch mode (Fig. 2) by a laboratory module EDR-Z/10-0.8 which contained 10 membrane pairs with cation exchange membranes CM-PES and anion exchange membranes AM-PES (MEGA, Czech Republic). The membranes parameters are listed in Table 1. The effective area of the membrane is 4 x 16 cm. A treated solution was prepared by a commercial fertilizer and demineralized water. Two litres of the treated solution were put into the diluate tank, 2 L into the concentrate tank and 0.25 L into the electrode solution tank. The circulation flow rates of diluate and concentrate were 70 L/h and voltage of 10 V was applied. Temperature was kept at 25 ± 1 °C. The tests were terminated after an achievement conductivity of 0.1 mS/cm in diluate.
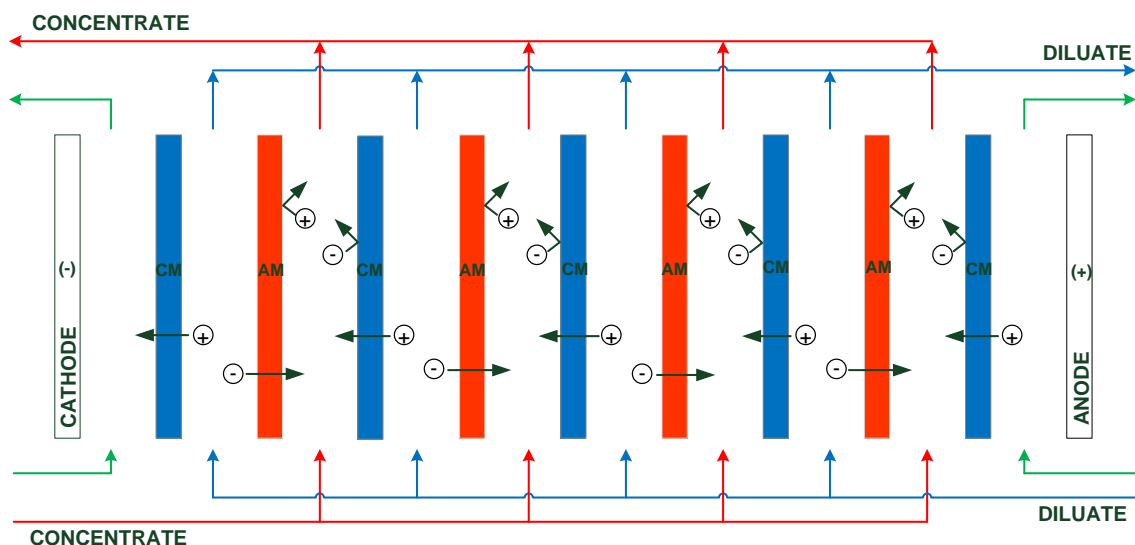
Figure 1. Principle of electrodialysis; CM – cation exchange membrane; AM – anion exchange membrane

Table 1. Membranes parameters

membrane	ion exchange group	thickness of swelled membrane	area resistance in 0.5 mol/L NaCl	transport number 0.5/0.1 mol/L KCl
		[mm]	[􀀀 cm	
CM-PES	$R\text{-}SO_3^-$	< 0.7	< 8	> 0.95
AM-PES	$R\text{-}(CH_3)_3N^+$	< 0.75	< 7.5	> 0.95

The second set of experiments was carried out in a batch mode by a pilot module EDR-Y/25-0.8 which contained 25 membrane pairs with cation exchange membranes CM-PES and anion exchange membranes AM-PES. The effective area of the membrane is 10 x 40 cm. The treated solution was used a real waste water from the fertilizer producer. Ten litres of the treated solution were put into the diluate tank, 10 L into the concentrate tank and 5 L into the electrode solution tank. The circulation flow rates of diluate and concentrate were 500 L/h and voltage of 25 V was applied. Temperature was kept at 25±1 °C. The tests were terminated after an achievement conductivity of 0.1 mS/cm in diluate.

The last set of experiments was carried out in a feed&bleed (Fig. 3) mode by the pilot module. This experiment was done with the real waste water on the producer site. The treated solution circulated through the diluate and concentrate chambers by 500 L/h. A constant concentration in diluate solution was kept by adding treated solution and excess of solution overflowed. Temperature was in range 20 – 25 °C and voltage of 25 V was applied.

Salt removal (SR) was a suitable parameter for evaluation of experiments. SR meant an amount of salts which were removed from feed solution in one pass through the module. SR was calculated from Eq. 1 if the water transport through the membranes is neglected.

$$SR = \frac{c_{IN} - c_{OUT}}{c_{IN}} \cdot 100\% \qquad\qquad (1)$$

c_{IN} and c_{OUT} are the concentrations at the inlet and the outlet of the diluate chamber.
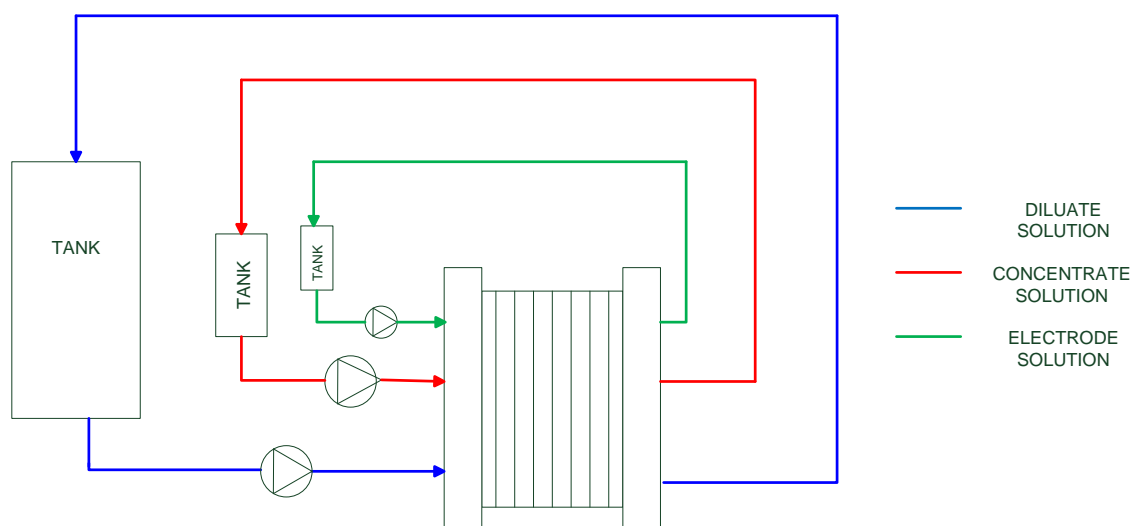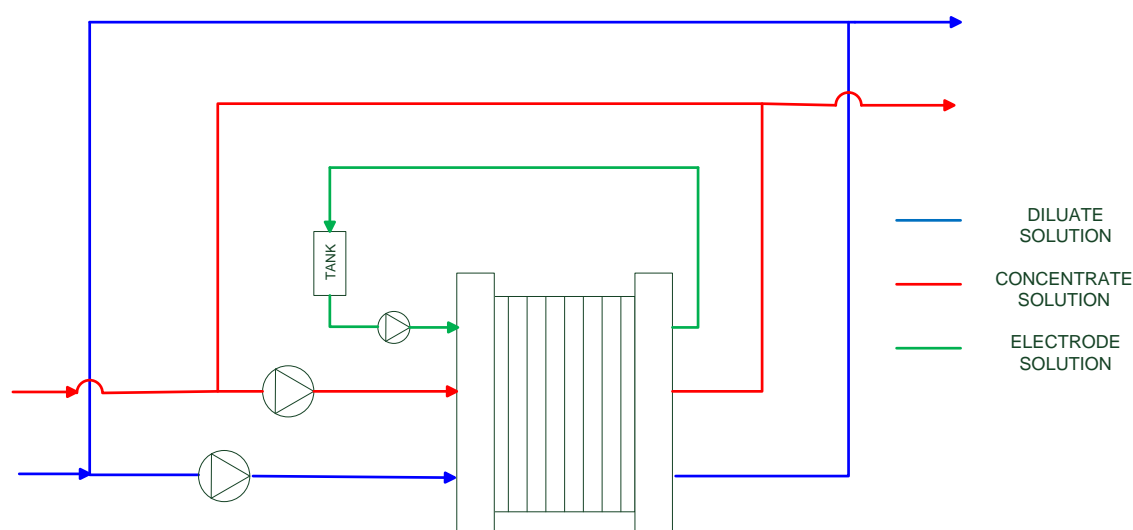
Figure 2. Scheme of the batch mode

Figure 3. Scheme of the feed&bleed mode

3. RESULTS AND DISCUSSION

3.1 Laboratory and pilot tests

The batch tests were carried out and SRs were calculated. Dependence of SR on the feed concentration of CN is shown in Fig. 4 for the laboratory and pilot ED. The lower concentration was, the higher SR was measured. A higher growth of the dependence for pilot was caused by longer desalting chamber. The longer desalting chamber meant higher delay inside the ED module and thus longer time for desalination. The concentration of concentrate was set by volumes and ration of the diluate and concentrate solutions. The values were 28 g/L and 35 g/L of CN for laboratory and pilot tests respectively.

The feed&bleed test with the real waste solution was done in order to the concentration in concentrate stream was not influenced by the diluate/concentrate volume ratio. In this case the concentration in concentrate was over 200 g/L of CN (Fig. 5). Although values of SR were lower than in the batch test, the dependence of SR on the feed concentration had the same shape (Fig. 6). Osmosis and electroosmosis between diluate and concentrate streams caused lower SR. Knowledge of SR is important for an industrial technology design.
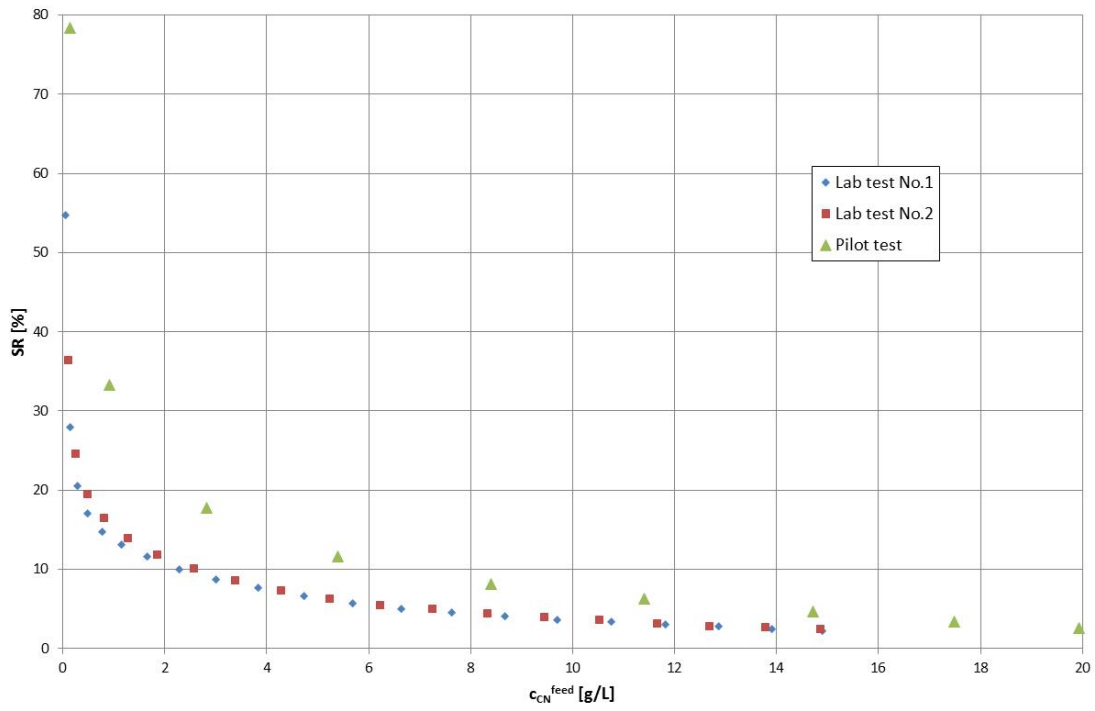
Figure 4. Dependence of salt removal on feed concentration of calcium nitrate, batch tests
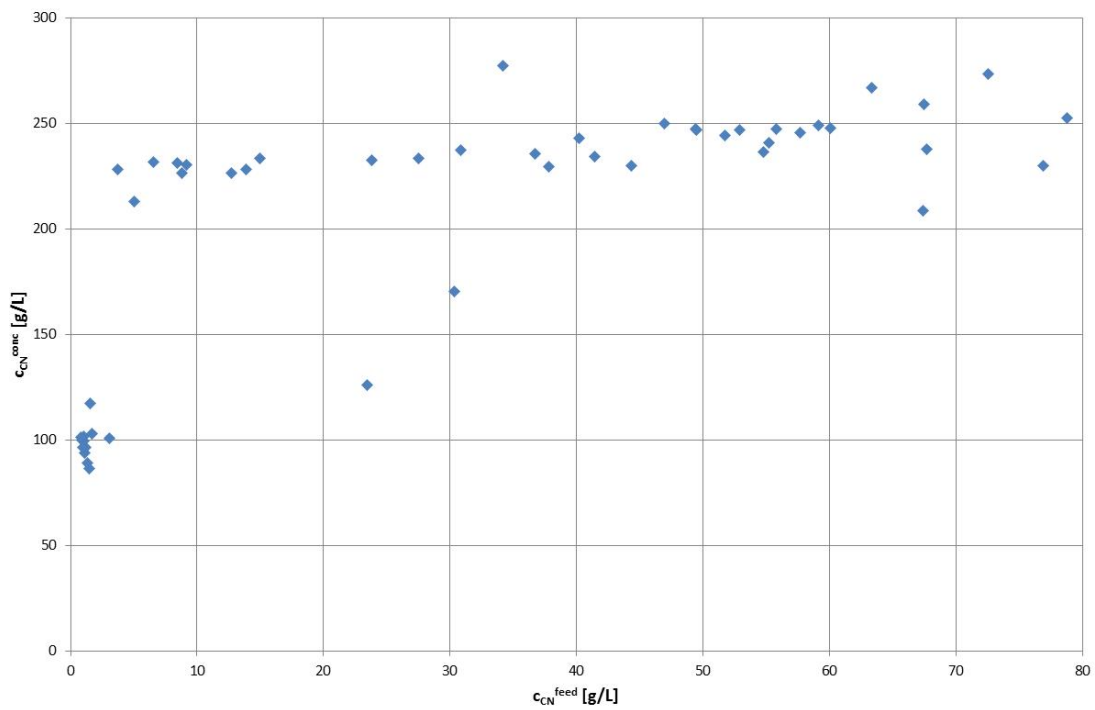

Figure 5. Dependence of CN concentration in concentrate stream on feed concentration of CN, feed&bleed test
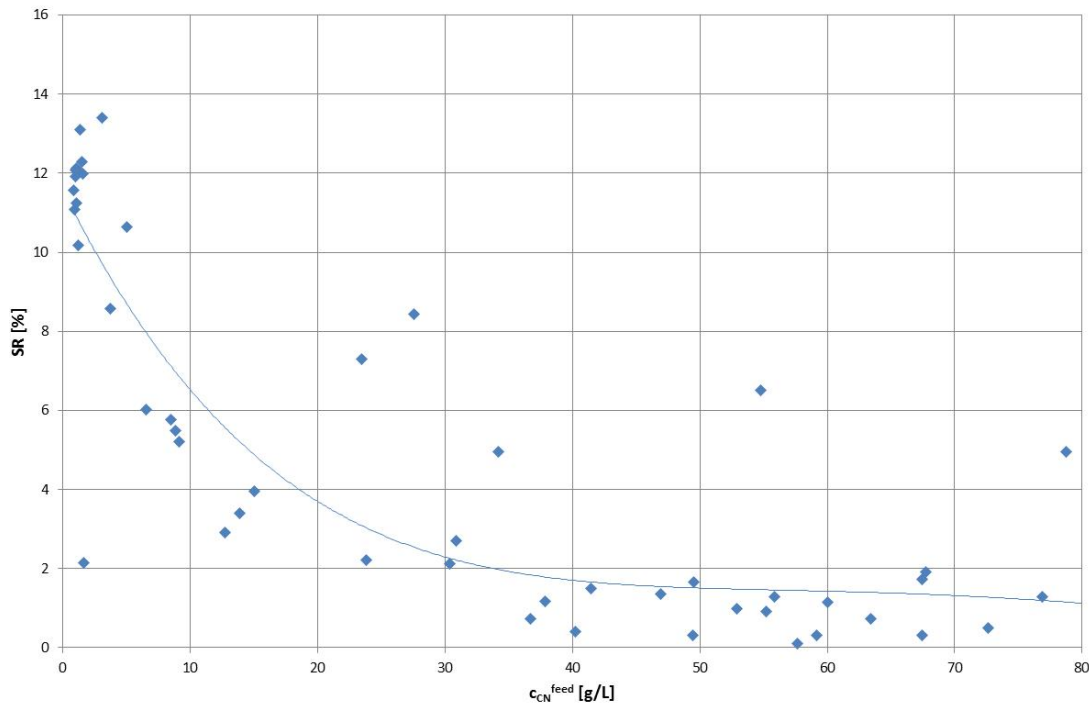
Figure 6. Dependence of salt removal on feed concentration of calcium nitrate, feed&bleed test

3.2 Industrial technology

Data from the feed&bleed test were used for the industrial technology design. The industrial technology had to satisfy the following conditions:

- capacity: 200 m^3/d

- inlet concentration: 42.5 g/L of CN

- temperature: 20 – 25 °C

- continuous operation

- target diluate concentration: 2.1 g/L of CN

- target concentrate concentration: maximum possible

The industrial technology would content 12 ED modules; type ED-II/250-0.8 (MEGA, Czech Republic). Each module consists of 250 membrane pairs with CM-PES and AM-PES ion exchange membranes. The operation mode would be batch due to the expectation of variable CN content in the waste solution. The concentration in the concentrate stream would be over 200 g/L of CN and energy consumption was calculated 0.45 kWh per 1 kg of solid CN.

4. CONCLUSION

Electrodialysis is very effective process for a reduction of waste water from the calcium nitrate production. Both laboratory and pilot tests confirmed a capability of ED to achieve the diluted and concentrated streams. It was possible to reach the concentration 200 g/L of CN in concentrate. All results were useful for the design of the industrial ED technology in the capacity of 200 m^3/d. The technology would content 12 electrodialysis modules ED-II/250-0.8.

5. ACKNOWLEDGEMENT

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