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Simultaneous regeneration of inorganic acid and base from a metal washing step wastewater by bipolar membrane electrodialysis after pretreatment by crystallization in a fluidized pellet reactor

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ABSTRACT

This study aims to investigate the feasibility of an integrated system consisting of a fluidized pellet reactor and bipolar membrane electrodialysis (EDBM) for regeneration of acid and base from wastewater with a high concentration of calcium and nickel ions. The fluidized pellet reactor was used to reduce the potential of scaling on the membranes by crystallization. EDBM was applied to regenerate acid/base from this pretreated wastewater. The results show that calcium and nickel can be removed by the fluidized pellet reactor with sufficient efficiency (74% and 73% without filtration, 74% and 94.4% with filtration, respectively). After pretreatment, it was feasible to regenerate mixed acid and base using EDBM. The current efficiency was 69% for the acid, 80% for the base; the energy consumption was 5.5 kW h/kg acid and 4.8 kW h/kg base at a current density of 60 mA/cm^2 and an initial concentration of 0.2 N. In a long-term experiment, the pretreatment increased cation exchange membrane performance and a high concentration of acid and base up to 1.76 N and 2.41 N was produced with only slight scaling on the cation exchange membrane surface. This integrated process is not only technically but also environmentally feasible, reducing water pollution and yielding valuable products to achieve sustainable development.

1. Introduction

Industrial wastewater from metal washing is a major concern due to its complex composition with sometimes high concentrations of a mixture of heavy metals and salts. Such wastewater can be treated by using physico-chemical methods to achieve the standard requirements before being discharged to the aquatic environment. However, a more sustainable solution may be to consider the wastewater as a 'renewable resource' from which water and other valuable substances can be reused or recovered for economical reasons and environment protection [1]. Bipolar membrane electrodialysis (EDBM) has been explored as a promising process to control water pollution and achieve sustainable development [2–4], which not only removes the salt from the wastewater but also produces acid/base from the corresponding salt. A bipolar membrane typically consists of two contacting, oppositely-charged ion exchange layers, producing hydroxide ions and protons that combine with cations and anions in wastewater to form acid and base, respectively [5,6]. EDBM can be used in several applications such as chemical processing (inorganic and organic acid/base production) [7–9], process integration (isolation of organic acids, food sector) [10,11] and pollution control (salt removal, acid/base regeneration) [12–14]. For acid/base regeneration from wastewater such as reverse osmosis (RO) concentrates [12] and spent caustic solutions [13], EDBM is thought feasible to split the salt in the wastewater into acid and base. Yang et al. reported the continuous regeneration of mixed acid and sodium hydroxide from RO concentrate up to 1 M at a current density of 57 mA/m^2, a flow rate of 0.3 L/h and total membrane surface of 264 cm^2. Two advantages were achieved: the produced acid was

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reused for RO system pretreatment and the contaminants were removed from RO concentrate to protect the aquatic environment [12]. Wei et al. regenerated sodium hydroxide from spent caustic stream of petrochemical industry [13] at a current density of 50 mA/cm^2, the effective membrane area of 7.07 cm^2 and an initial base concentration of 0.1 M. They showed that the current efficiency was over 90% at an energy consumption of 8.2 kW h/kg NaOH and a process cost of 0.97 USD/kg NaOH. The authors remarked that if the cost of bipolar membrane was reduced, EDBM would become more economically competent.

Recovering acid/base from industrial wastewater with high concentration of salt and metals ions not only brings benefits to the environment, reduces water pollution but also yields valuable products for sustainable development. Although the principle to produce acid and base of the EDBM process is always the same, the applications are different for every case since the feed streams are not pure: they contain a mixture of other contaminated components from production processes which leads to challenges in industrial application [2]. One of the difficulties for acid/base recovery by EDBM is scaling on the membrane, due to the high concentration of multivalent ions such as calcium, magnesium, nickel, etc. in the wastewater. For RO concentrate as feed to produce acid and base, various methods have been explored to prevent scaling by using ion exchange to reduce the concentration of divalent ions prior to EDBM on lab scale, and lime softening on full scale [15]. Previous studies showed the feasibility of applying a fluidized pellet reactor for calcium removal from RO concentrate [16] and also from industrial washing-step water [17] with a high efficiency of up to 90%. Thus, the hypothesis in this study is that a fluidized pellet reactor may allow for a smooth operation of EDBM for challenging wastewaters, by removing scalants prior to EDBM. Industrial wastewater with a high concentration of calcium, sodium and sulfate comes from an industrial Ni processing plant in Belgium. Some additional nickel is added. This wastewater was pretreated by a fluidized pellet reactor and then fed to EDBM to regenerate H_2SO_4 and NaOH. The objective was to investigate the efficiency of pretreatment by a fluidized pellet reactor for calcium and nickel removal prior to EDBM, to study the effect of the operational conditions on the efficiency of acid and base regeneration from the pretreated industrial wastewater by EDBM and to evaluate the effect of scaling on the membrane surface when operated in a long-term experiment.

2. Materials and methods

2.1. Reagents and membranes

The following reagents were used in the experiments: H_2SO_4 97% (Merck, Germany), HNO_3 56% (Chem-Lab, Belgium), HCl 0.1 N, NaOH 0.1 N, NaOH (solid), Na_2CO_3 (Fisher Scientific, UK), Na_2SO_4 (Sigma-Aldrich, Belgium), $CaCl_2 \cdot 2H_2O$, $NiSO_4 \cdot 6H_2O$ (Chem-Lab, Belgium) and de-ionized water (Millipore Milli-Q 18 MΩ). Cation exchange membranes (FKB), anion exchange membranes (FAB) and bipolar membranes (FBM) were obtained from Fumatech GmbH (Germany). The characteristics of the three kinds of membranes are presented in Table 1.

2.2. Wastewater and its pretreatment

The industrial wastewater considered in this investigation comes from an industrial Ni processing plant in Belgium, to which nickel is added; the composition of the raw wastewater is shown in Table 2.

Due to the high concentration of calcium and nickel in the wastewater, precipitation of these ions with hydroxide in the base compartment may easily result in scaling on membrane surfaces during operation. Therefore, the wastewater was pretreated by crystallization in a fluidized pellet reactor described elsewhere [16,17] with the following operational conditions: flow rate Q of 14 L/h, molar ratio R of CO_3^{2-} to Ni^{2+} and Ca^{2+} in a range from 2 to 8 and NaOH dose in a range from 0.2 to 0.8 g/L wastewater. The fluidized pellet reactor consisted of a 2 cm diameter glass column of 2.2 m high filled with 0.55 m of garnet sand (400 g, 150–300 μm; mean value 160 μm) from Minelco, Germany as seed material (Fig. 1). In the top, the reactor has a larger diameter in order to decrease the velocity of the effluent and to prevent the sand from being dragged out. During the operation, the wastewater was pumped vertically upward through the seeding without recirculation at the suitable velocities to obtain the fluidized bed in the pellet reactor. At the same time, a mixed solution of sodium hydroxide and sodium carbonate was injected at the point 3 cm away from the bottom of the fluidized pellet reactor with a flow rate of 1 L/h to adjust the pH and to add carbonate into the wastewater in order to have the reactions (2), (3) and (4). The injected amount of Na_2CO_3 and NaOH depended on the molar ratio R and NaOH dose.

All tests were performed within a 6 h continuously operating period. To maintain calcium and nickel concentrations and the pH described above, treated water in the fluidized pellet reactor was reused after adding $CaCl_2 \cdot 2H_2O$, $NiSO_4 \cdot 6H_2O$, and adjusting the pH with HNO_3 (56%) and NaOH (6 M). The following reactions

Table 2
Composition of the industrial wastewater.

Parameters	Units	Raw wastewater	Pre-treated wastewater	Feed solution for EDBM
Calcium	mg/L	90–120	27–28	16–17
Nickel	mg/L	40–60	14–15	10–11
Sodium	mg/L	41,530–47,150	41,530–47,150	41,530–47,150
Strontium	mg/L	3.5–5	2.1–2.6	1.9–2.1
Iron	mg/L	0.57–1.0	0.5–0.67	0.77
Chromium	mg/L	0.028–0.03	0.033	0.04
Sulfate	mg/L	84,700–88,560	75,940–89,220	75,940–89,220
Conductivity	mS/cm	84–86	82–86	82–86
pH	–	6.7–6.8	10.3–10.9	10.3–10.9

Table 1
Characteristic of the membranes.

Membrane	Thickness (mm)	Ion exchange capacity (meq/g)	Chemical stability (pH)	Water splitting[a]/selectivity[b] (%)	Swelling (%)	Surface potential (Ω cm^2)
FKB	0.1–0.12	1.01	4 M KOH	98.2[b]	22	4.25
FAB	0.09–0.11	1.12	11–12% H_2SO_4	97.1[b]	15	5.7–6.2
FBM	0.18–0.2	–	1–14	> 98[a]	–	< 3

[a] Water splitting for bipolar membrane.
[b] Selectivity 0.1/0.5 mol/kg KCl at $T = 25$ °C for cation and anion exchange membrane.