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Regenerating sodium hydroxide from the spent caustic by bipolar membrane electrodialysis (BMED)

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ABSTRACT

An experimental study was carried out on regeneration sodium hydroxide (NaOH) from the spent caustic by bipolar membrane electrodialysis (BMED). The effects of operation parameters, such as concentration of electrolyte, current density and initial base concentration, on regeneration were investigated. The results indicate that low energy consumption and high current efficiency can be achieved with the concentration of electrolyte in the range of 0.20–0.30 mol/L, initial concentration of the base in range of 0.10–0.25 mol/L and current density in the range of 30–60 mA/cm^2. The process cost is estimated to be USD 0.97 for regenerating 1 kg NaOH with the laboratory-scale equipment, showing economically competitive.

1. Introduction

Spent caustic is a common waste that is produced from chemical industries such as ethene plants, refineries, etc. Spent caustics are generally odorous with high pH and high concentration of sulfides and organics. They should be treated properly before discharged to sewage systems to avoid deactivation of microorganisms.

At present, one practical treatment method is neutralization with acids [1]. A large number of acids are consumed to quench caustics which in fact are potentially recyclable. Alternatively, spent caustics could be treated by chemical oxidation and precipitation [2–3], etc. However, these techniques are of commonly low removal efficiency and high expense, and in some cases cause second pollution.

In allusion to the features of caustic wastewaters, bipolar membrane electrodialysis (BMED) provides an attractive caustic recovery method with environmental benignity. BMED is a combination of the conventional electrodialysis and water dissociation of bipolar membrane. It can split water into H^+ and OH^- under a reverse bias of direct current field and thus can be used to recycle valuable components from wastes by providing the acid or base sources in situ [4–6]. Due to its high efficiency, environmental benignity and operational simplicity, this technology has been exploited to apply in many fields, for example, organic acid production [7–10], environmental protection [11–14], organic amine production [15–18] and electroacidification and electroalkalization [19,20], etc.

The principle of caustic recovery by BMED is shown in Fig. 1. Sodium ion (Na^+) in the spent caustic migrates through the cation-exchange membrane to the base compartment, where it combines with hydroxide ions (OH^-) produced by the bipolar membrane to generate sodium hydroxide (NaOH). This technique not only makes full use of the recyclable bases, but also limits the usage of acids. It has technical advancements and economical competence. However, so far little operational data has been published on this topic. Therefore, the objective of this study is to test the feasibility of regenerating sodium hydroxide from spent caustic by using BMED. The operational parameters, such as electrolyte concentration, initial base concentration and the current density, were examined with regard to process efficiency and the product yield.

2. Experimental

2.1. Materials

Membranes used in the experiments were Neosepta BP-1 (bipolar membrane, Tokuyama Co., Japan) and Neosepta CMX (cation exchange membrane, Tokuyama Co., Japan). Their properties were listed in Table 1. All chemicals were of analytical grade and used as received. Distilled water was used throughout.

2.2. Apparatus

Sodium hydroxide recovery from spent caustic can be performed with BP-C, BP-A and BP-C-A. But with BP-A configuration, the recovered base still coexists with feed wastewater and a pure

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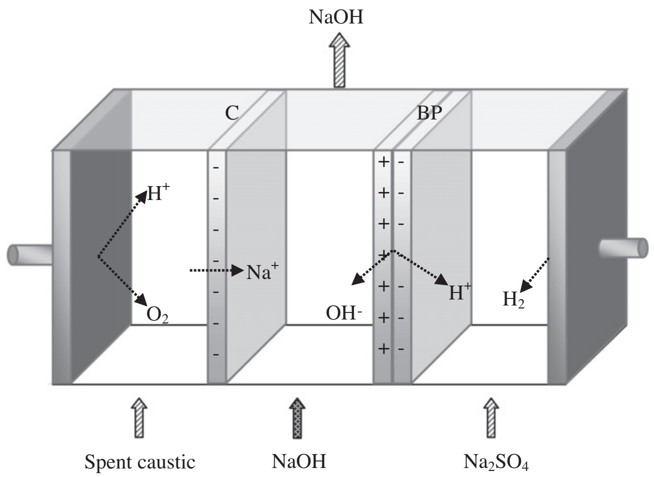

Fig. 1. Schematic of BMED system operating principle. (BP, bipolar membrane; C, cation exchange membrane).

Table 1
Properties of the membranes applied to the BMED stacks[a].

Membrane	Thickness (μm)	IEC (meq g^{-1})	Area resistance (Ω cm^2)	Voltage drop (V)	Efficiency (%)
Neosepta BP-1	200–350	–	–	1.2–2.2	>98
Neosepta CMX	220–260	1.5–1.8	2.0–3.5	–	–

[a] The data are collected from the product brochure provided by the company.

alkali cannot be obtained. With BP-C-A configuration, the energy consumption and process cost will increase because it uses more membranes compared with two-compartment BP-A or BP-C cell configuration. Based on this consideration, the electrodialysis experiments were conducted with BP-C compartment. Fig. 1 illustrates the configuration of the BMED stack applied in the experiment. Specifically, the stack is comprised of (a) a cathode and an anode, which are made of titanium coated with ruthenium, (b) a cation exchange membrane and a bipolar membrane, which each has an effective membrane area of 7.07 cm^2. The stack had three compartments. Each compartment was formed by a spacer made of Plexiglas with thickness of 1 cm. Both electrodes were connected with a direct current power supply (WYL1703, Hangzhou Siling Electrical Instrument Ltd.). Each compartment was connected to a 500 mL beaker, allowing recirculation of external solutions by submersible pumps (AP1000, Zhongshan Zhenghua Electronics Co. Ltd., China, with the maximal speed of 27 L/h). In this experiment, a Na_2SO_4 solution (0.15–0.35 mol/L, 250 mL) was used as the supporting electrolyte solution in cathode chamber. The anode chamber was fed with the spent caustic (250 mL), and the central chamber was fed with a NaOH solution (250 mL), respectively. Before an electric current was applied, the solution of each compartment was recirculated for half an hour, and all the visible gas bubbles were eliminated.

2.3. Wastewater and chemical analysis

The spent caustic was obtained from Research Institute of Daqing Petrochemical Company, PetroChina. The concentration of NaOH and Na_2CO_3 was determined by a double indicator method with phenolphthalein and methyl orange as indicators. The concentration of Na_2SO_4 was determined by ICP-OES. The results were shown in Table 2. The concentration of recycled NaOH in the base compartment was determined by titration with phenolphthalein as an indicator.

Table 2
The main compositions of the spent caustic.

Component	Concentration (mol/L)
NaOH	0.440
Na_2CO_3	0.290
Na_2SO_4	0.048
Oil	Seldom

For comparison, a simulated caustic solution was also prepared according to the main compositions in Table 2 but without oil.

2.4. Calculation of current efficiency and energy consumption

The current efficiency η (%) was calculated in Eq. (1) [21]:

$$\eta = \frac{(C_t - C_0)VF}{It} \tag{1}$$

where C_t and C_0 (mol/L) are the concentrations of NaOH at time t and 0, respectively; V (L) is the recirculated volume of solution in the base cycle; F is the Faraday constant (96485 C mol^{-1}); and I (A) is the current. Since the volume change of solutions fed to each compartment was negligible during operation, V was equal to 0.25 L throughout.The energy consumption E (kWh kg^{-1}) was calculated in Eq.(2) [21]:

$$E = \int \frac{UIdt}{C_t VM} \tag{2}$$

where U (V) is the voltage drop across the BMED stack, I (A) is the current, C_t (mol/L) is the concentration of NaOH at time t, V is the volume of the base cycle (0.25 L), and M is the molar mass of sodium hydroxide (40.00 g mol^{-1}).

All the experimental data were averaged from three independent experiments. The error was calculated to be approximately ±5%.

3. Results and discussion

3.1. Effect of concentration of electrolyte on the sodium hydroxide regeneration

Fig. 2a shows the effect of concentration of electrolyte Na_2SO_4 on voltage drop across the membrane stack. The voltage drop across the stack decreases with an increase in the Na_2SO_4 concentration. Here, Na_2SO_4 acts as a supporting electrolyte. It is logically true that the higher the Na_2SO_4 concentration is, the lower electrical resistance there will be. When it comes to the each curve, there is a slight increase in the voltage drop at the beginning, which is due to ions depleted in the intermediate layer of bipolar membrane and electric resistance of the bipolar membrane increased [22,23]. Afterwards the voltage drop decreases, indicating that OH^- and H^+ produced by the water dissociation in the intermediate layer of bipolar membrane increase greatly and the electrical resistance decreases.

Fig. 2b demonstrates the change of sodium hydroxide yield with electrolyte concentration. It can be observed that sodium hydroxide yield has not been affected significantly by electrolyte concentration except that it increases with operation time. It indicates that the hydroxide ions (OH^-) produced by the bipolar membrane increases.

Fig. 2c shows the effect of electrolyte concentration on energy consumption and current efficiency. It can be observed that the energy consumption decreases as the electrolyte concentration increases. The reason is that the electrical resistance of the stack decreases as the electrolyte concentration increases. However, with the electrolyte concentration increasing further, the ratio of the solution resistance to the total membrane stack resistance