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Facile recovery of acetic acid from waste acids of electronic industry *via* a partial neutralization pretreatment (PNP) – Distillation strategy

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ABSTRACT

In recent years, attention on treatment of industrial waste acids has been increasing considerably due to enforcement of the environmental regulations as well as economical considerations about the waste acids. In this paper, a novel approach for recovery of acetic acid (HAc) from electronic industrial waste acids, containing about 58 wt.% of HAc, 39 wt.% of nitric acid (HNO_3), 3 wt.% of phosphoric acid (H_3PO_4), and small amount of hydrochloride acid (HCl) and hydrofluoride acid (HF), was developed using partial neutralization pretreatment (PNP)-distillation strategy. The effects of distillation time, types of alkali for neutralization and oil bath temperature on recovery of HAc were systematically studied. It was found that HAc can be efficiently recovered from the waste acids with a yield of 94.3% (purity 99.4%) under optimal conditions. The treatment scheme for HAc recovery from waste acids is featured by feasibility, reproducibility and massive productivity.

1. Introduction

With the rapid growth of economy, China's electronic industry has been booming in recent years, resulting in the production of a large number of waste acids, which are mainly composed of acetic–nitric–phosphoric acids in the process of etching and cleaning. Therefore, much attention has been paid to the treatment of industrial waste acids due to enforcement of environmental regulations as well as economical consideration into waste acids [1].

There are increasing demand for HAc worldwide, and China accounts for more than 40% of world's consumption of HAc in 2012 [2]. Unfortunately, most of the waste acids containing HAc were disposed of by simple neutralization, which poses potential environmental hazards and financial burdens. Therefore, recovery or reuse of acetic acid from the waste acids is of great importance and urgently needed from the viewpoint of sustainable development.

Up to now, various technologies have been developed for acid recovery, including diffusion dialysis [3–5], electrodialysis [6], pervaporation [7–9], crystallization [10,11], esterification [12] and extraction [13,14]. Recently, some hybrid separation schemes have also been proposed, such as a combination of diffusion dialysis and vacuum distillation [15], and a combination of cloud point extraction and complex extraction [16]. However, recovery of HAc from waste acids generated from the etching process in the electronic industry has seldomly been reported. Shin and Kim [17,18] studied the recovery of HAc from waste acids generated in semiconductor wafer production using solvent extraction. Although a relatively high recovery efficiency of HAc was achieved, there are some apparent disadvantages for this approach, including high costs due to loss and regeneration of the extraction solvent, huge amount of water consumption and the required raffinate treatment.

In this paper, we report the development on innovative approach in recovery of HAc from etching waste acids of electronic industry *via* a combination strategy of partial neutralization pretreatment (PNP) and subsequent distillation. The composition in the waste acids shown in Fig. 1. It can be seen that HAc and HNO_3 account for about 97 wt.% of the acids (58 wt.% for HAc and 39 wt.% for HNO_3). Considering that HAc is a weak acid ($K_a = 1.8 \times 10^{-5}$) when compared with HNO_3 and the boiling point of HAc (118 °C) is much lower than that of HNO_3 (83 °C), HAc may be efficiently separated from the waste acids by simple distillation after neutralization of HNO_3. It should be noted that after neutralization, almost all of the acid converted to their corresponding salts except for HAc through a proper dosage of alkali. This is the reason why waste acids can only be partially neutralized. The experimental parameters such as distillation time, types of alkali for neutralization and oil bath temperature on recovery of HAc were systematically investigated in this study.

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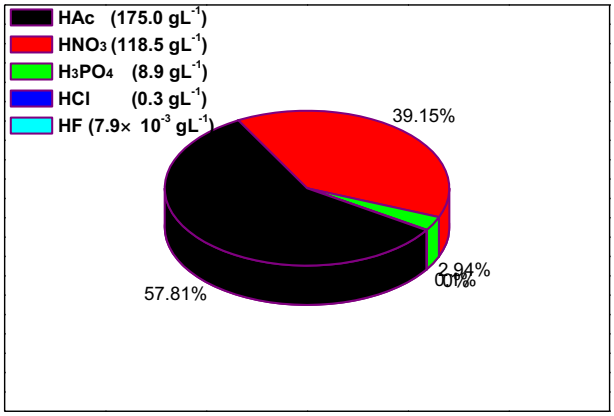

Fig. 1. Compenents of waste acids from electronic industry.

2. Materials and methods

2.1. Materials

Waste acids used in this study was acquired from T-Electronic Manufacture Factory in Hubei province of China, and the corresponding chemical composition in waste solution was shown in Fig. 1. It can be seen the main components were HAc and HNO_3 with a small amount of H_3PO_4, and trace amounts of HCl and HF. All chemicals used in this study were from Sinopharm Chemical Reagent Co., Ltd., China.

2.2. Analysis

The concentrations of HAc and HNO_3 were analyzed by a total organic carbon/nitrogen analyzer (Multi N/C 3100, Analytikjena, Germany), while the concentrations of H_3PO_4, HCl and HF were measured by ion chromatography (ICS-2100, Thermo Scientific, America).

2.3. Part neutralization pretreatment

Neutralization was carried out in a 250 mL glass beaker containing 150 mL of the mixed waste acids. Approximately 1.02 equivalents of the theoretically required alkali to HNO_3 was added to the solution for neutralization under continuous agitation at room temperatures.

2.4. Distillation

150 mL of the pretreated solution was transferred into a 250-mL round-bottom flask followed by distillation using as oil bath (liquid paraffin).

3. Results and discussion

Separation efficiency of HAc was evaluated by the volume of distillate and the purity (p) of HAc in the distillate, which can be expressed by Eq. (1):

$$p = \left(\frac{C_{fr}^{H}}{C_{fr}^{H} + C_{fr}^{N} + C_{fr}^{P} + C_{fr}^{F} + C_{fr}^{Cl}}\right) \times 100\% \quad (1)$$

where V_{fr} is the volume of the distillate, C_{fr}^{H}, C_{fr}^{N}, C_{fr}^{P}, C_{fr}^{F} and C_{fr}^{Cl} are concentrations of HAc, HNO_3, H_3PO_4, HF and HCl in the distillate, respectively.

Compared to HAc and HNO_3, the concentrations of H_3PO_4, HF and HCl in the waste acid were much smaller. Therefore, Eq. (1) can be simplified to (2):

$$p = \left(\frac{C_{fr}^{H}}{C_{fr}^{H} + C_{fr}^{N}}\right) \times 100\% \quad (2)$$

The recovery rate (R) of HAc can be calculated from Eq. (3) below [18]:

$$R = \frac{V_{fr}C_{fr}^{H}}{V_{fe}C_{fe}^{H}} \times 100\% \quad (3)$$

V_{fe} is the volume of the waste acid, C_{fr}^{H} and C_{fe}^{H} are concentrations of HAc in the distillate and the waste acid, respectively.

HAc and a small amount of HNO_3 were detected in distillate when waste acids were distilled directly. Fig. 2 showed the effect of distillation time on recovery of the waste acids. It was found that only HAc and HNO_3 were detected in the distillate, and with an extension of the distillation time from 2 to 6 h, the recovery rate increased from 43.5 to 72.9 wt.% and from 4.2 to 10.0 wt.% for HAc and HNO_3, respectively. Although the boiling point of HAc (118 °C) is much higher than that of HNO_3(83 °C), direct distillation cannot make them efficiently separated.

3.1. Effect of partial neutralization pretreatment

Since HAc is a weaker acid (dissociation constant, $K_a = 1.8 \times 10^{-5}$) when compared with HNO_3, HNO_3 is easier to be neutralized in the presence of a base. By precise control the amount of alkali, it is possible to neutralize all of the HNO_3 in solution while HAc was kept in an acid form. Then HAc can be easily separated from solution without the interference of HNO_3. To make sure that almost all of the HNO_3 were neutralized in solution, alkali with 1.02 equivalent weight corresponding to HNO_3 were added before distillation. Fig. 3 compares the effects of four types of alkali, namely NaOH, KOH, $Ca(OH)_2$ and CaO, on the recovery of HAc at 140 °C with a distillation time of 5 h. As expected, it was found that only HAc (without any HNO_3) was detected in distillate, reflecting the importance of the PNP process. The recovery rate of HAc were calculated to be 94.3, 93.0, 83.2 and 79.3 using NaOH, KOH, $Ca(OH)_2$ and CaO as alkali, respectively. Consequently, NaOH was used to neutralize the waste acids in the subsequent experiments during PNP (12.2 g NaOH in 150 mL of waste acids).

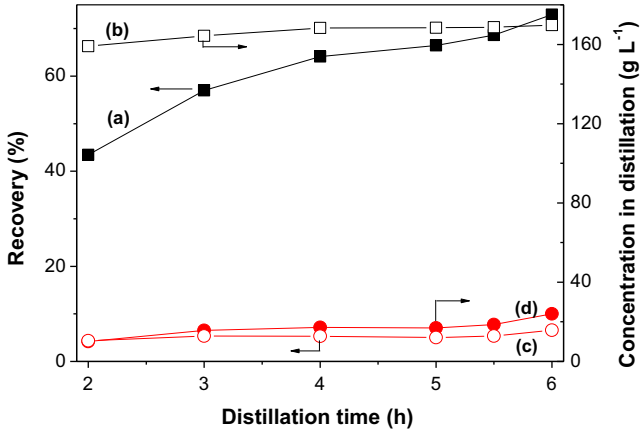

Fig. 2. Dependence of distillation time on the recovery rate (a and c) and concentration (b and d) of HAc (a and b) and HNO_3 (c and d) in the distillate.