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Influence of the diluent on the extraction of acetic acid from the prehydrolysis liquor of kraft based dissolving pulp production process by tertiary amine

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ABSTRACT

Different diluents including 1-decanol, 1-octanol and 2-ethyl-1-hexanol and kerosene have been evaluated in extracting acetic acid from the treated prehydrolysis liquor (TPHL) by triisooctylamine (TIOA) or trioctylamine (TOA). Diluent played an important role in recovering acetic acid from the TPHL, thus affecting the extraction equilibrium and extraction efficiency. Polar diluent like 1-decanol, 1-octanol and 2-ethyl-1-hexanol showed better performance than the nonpolar diluent kerosene. The maximum extraction efficiency was 68.79%, which was from 2-ethyl-1-hexanol. The organic solvent was regenerated and extracted HAc was recovered by aqueous sodium hydroxide. The regeneration efficiency can be improved by increasing molar ratio of sodium hydroxide to HAc.

1. Introduction

It is now well established that the pre-hydrolysis liquor (PHL) of dissolving pulp production process is a good feedstock of a lignocelluloses biorefinery [1–4]. Acetic acid is one of the main components in the industrial PHL from a hardwood kraft-based dissolving pulp production process [3,5] and its concentration is about 1%. The recovery of acetic acid from the PHL is a promising opportunity in the path of green economy, and it can be recovered by distillation, liquid–liquid extraction, adsorption, membrane separation etc. For the distillation method, the dilute nature of the PHL would lead to very high energy cost. The reactive extraction was selected for the present investigation in considering its efficiency and selectivity from such a dilute solution [4].

It is reported that tertiary amine is the better extractant for the removal and recovery of carboxylic acid from industrial waste water [6–10]. Diluent is usually added along with the extractant to improve extraction power of the extractant by providing solvation and specific interaction. It was observed that the extraction efficiency of amine in the reactive extraction was significantly affected by the type of diluents [11]. Therefore, it is important to select an efficient diluent to improve extraction efficiency. The diluent may consist of one or more components, including aliphatic/aromatic hydrocarbons, ketones, higher alcohols. Sahin et al. [12] investigated the extraction of formic acid by a high molecular-weight aliphatic amine, tridodecylamine (TDA), and a phosphorus-bonded, oxygen-containing extractant, tributyl phosphate (TBP), dissolved in five different diluents (ethyl valerate, diethyl adipate, diethyl sebacate, 1-octanol, and heptane) and observed that combination of TDA and diethyl adipate had the highest distribution coefficient of 6. Tuyun and Uslu [13] studied different high alcohols, acetates, ketones for extracting picolinic acid by tridodecylamine and obtained the highest distribution coefficient for 1-octanol. Keshav et al. [14] investigated different diluents (*n*-heptane, petroleum ether, ethyl acetate and oleyl alcohol) for extracting propionic acid from a dilute aqueous solution by TOA. The highest extraction was found with TOA-oleyl alcohol. Qin et al. [15] studied on the extraction of different carboxylic acids by TOA in 1-octanol, chloroform, MIBK, tetrachloromethane and hexane to observe the effect of acid and effect of diluents. Extraction of different carboxylic acid using tri-*n*-butyl phosphate (TBP), tri-*n*-octyl amine (TOA) and their mixtures was investigated by Matsumoto et al. [11] and the synergism effect was highlighted

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in improving the extraction. For extracting acetic acid from the PHL, a suitable extraction and diluent need to be selected for getting maximum distribution coefficient.

The main objective of this work was to evaluate the different diluents namely 1-decanol (D), 2-ethyl-1-hexanol (E), 1-octanol (O) and Kerosene (K), and mixture of D and K, E and K for extracting acetic acid from the PHL of the kraft based dissolving pulp production process. Two types of extractant: Trioctylamine (TOA), and triisooctylamine (TIOA) were assessed. The extracted acetic acid was also recovered and solvent was regenerated by sodium hydroxide stripping.

2. Experimental

2.1. Materials

The industrial produced PHL sample was collected from the dissolving pulp mills in Eastern Canada. The PHL was filtered with Whatman qualitative filter papers and Nylon 66 membrane with a pore size of 0.45 μm (Supelco analytical group, USA) for removing large particles and impurities. Triisooctylamine (TIOA), trioctylamine (TOA), 2-ethyl-1-hexanol, 1-octanol, 1-decanol and kerosene were purchased from Sigma–Aldrich Co. (USA). CR325 W activated carbon was obtained from Carbon Resources Inc. (CA). Sulfuric acid was purchased from Fisher Scientific Inc. (USA). Sodium hydroxide (60 %wt) was obtained from Ricca Chemical Company (USA) and diluted to 5–30 %wt. for use.

2.2. Activated carbon treatment

The PHL was treated with activated carbon (AC) at room temperature and in sonication for 30 min. The weight ratio of PHL to AC was 20:1.

2.3. Sugar analysis

The sugar content of the PHL was determined by using an Ion Chromatography unit equipped with CarboPac TM PA1 column (Dionex-300, Dionex Corporation, USA) and a pulsed amperometric detector (PAD). The details methods are described in elsewhere [16,17].

2.4. Acetic acid and furfural analysis

A Varian 300 NMR–spectrometer was employed for determining the furfural and acetic acid concentrations as methods described earlier [17].

2.5. Lignin analysis

The UV/Vis spectrometric method at a wavelength of 205 nm (Tappi UM250) was used to measure the lignin content of PHL [16].

2.6. Liquid–liquid extraction

Required amount of the organic phase (tertiary amine and diluent or solvent) and aqueous solution (AC treated PHL samples) were charged in flasks separately. A extraction was performed by stirring by magnetic bar with heating at 400 rpm or shaking by shaker with heating at 200–300 rpm and varied temperature of 25–50 °C for the varied time of 5–15 min, and pH value of the AC PHL–amine mixture was adjusted by adding NaOH. Then the extraction mixture was centrifuged at 3000 rpm for 5 min to assist separation of organic and aqueous phases. The two phases were analyzed immediately after separation.

Amine concentration was defined the percentage of corresponding amine by mass balance

$$\%\text{Amine concentration} - \frac{W_{amine}}{W_{amine} + w_{Diluent}} \times 100\% \quad (1)$$

The concentration of HAC in organic phase was determined by mass balance

$$\left([HA]_{org}\right)_{eq} = \frac{\left([HA]_{aq}V_{aq}\right)_{initial} - \left([HA]_{aq}V_{aq}\right)_{eq}}{(V_{org})_{aq}} \quad (2)$$

where V_{aq} is the volume of aqueous phase (mL) and V_{org} is the volume of organic phase (mL).

For the evaluating extraction efficiencies of different runs, HAC recovery (%) and distribution coefficient (K_D) were introduced. The percent weight of HAC transferred from the aqueous phase into organic phase was expressed the percentage recovery of corresponding HAC.

$$\%\text{Recovery} = \frac{([HA]_{org}V_{org})_{aq}}{([HA]_{aq}V_{aq})_{initial}} \times 100\% \quad (3)$$

The equilibrium distribution coefficient (K_D) was defined the ratio of the HAC weight fraction of organic phase ($\lfloor HA \rfloor_{org}V_{org}$) to that of aqueous phase ($\lfloor HA \rfloor_{aq}V_{aq}$) , at equilibrium.

$$K_D = \left(\frac{[HA]_{org}V_{org}}{[HA]_{aq}V_{aq}}\right)_{eq} \quad (4)$$

2.7. Regeneration of tertiary amine and solvent/diluent

The regeneration of amine and solvent/diluent was done by adding aqueous sodium hydroxide in organic phase for 20–90 min at 1–4 M ratio of sodium hydroxide to HAc and shaking speed 200 rpm. Recovery of HAc by NaOH is based on the concentration of HAc in organic phase (Eq. (2)). The percent weight of HAc transferred from the organic phase into aqueous phase (sodium acetate) was expressed the percentage recovery of corresponding HAc.

$$\%\,\text{Recovery} = \frac{\left([HA]_{aq}V_{aq}\right)_{eq}}{\left([HA]_{org}V_{org}\right)_{initial}} \times 100\% \quad (5)$$

3. Results and discussion

3.1. Effect of different diluents for tertiary amine

Diluent for tertiary amine plays an important role in the extraction process [9,11,18,19]. Therefore, selection of a suitable diluent is an important factor for extracting acetic acid from the PHL. Fig. 1 shows the extraction equilibrium of acetic acid from the TPHL by TIOA in different diluents at the mole ratio of 1. The degree of extraction of acetic acid with TIOA was in the order of 2-ethyl-1-hexanol (E) > E + 1-octanol (O) > 1-decanol (D) > D + E > D + O > O > E + kerosene (K) > D + K > K. The maximum extraction of 68.79% was obtained for 2-ethyl-1-hexanol while the minimum extraction was 13.36% only for kerosene. The lower extraction equilibrium of kerosene can be increased to 53.13% and 52.92% with the addition of decanol or 2-ethyl-1-hexanol in kerosene, respectively.

The above results that polar diluents like 1-decanol, 1-octanol and 2-ethyl-1-hexanol showed better performance in recovering acetic acid from the TPHL when extracted using TIOA, than the nonpolar diluent can be explained as follows. The salvation of