Adsorption of Ionic Liquids from Cellulosic Hydrolysate by Ion-exchange Resin

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Abstract—Ionic liquids (ILs) have got wide applications as solvent or catalyst for the conversion of saccharides into valuable chemicals due to their fascinating properties. However, some ILs inevitably occur in separation difficulty from products in aqueous samples since they do have notable solubility in water. Meanwhile, it will bring about effluent discharges. Recently, the hydrolysis of cellulose in ionic liquids has been intensively investigated, but little is known about the ionic liquids removal from the hydrolysate. This study proposes adsorption by ion-exchange resin for the removal of ILs, involved in cellulosic hydrolysate. The ion-exchange resin of 732H with sulfonic acid functional group was applied to examine the sorption abilities for 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), 1-propyl sulfonic acid-3-methylimidazolium hydrogensulfate ([C₅SO₃Hmim]HSO₄) and benzothiazolium methanesulfonate ([HBth]CH₃SO₃H). The results showed that the resin of 732H exhibits promising sorption abilities for [Bmim]Cl and [HBth]CH₃SO₃H, while no sorption on [C₅SO₃Hmim]HSO₄. The static desorption experiment of ionic liquids was investigated, the results indicated that 92.05% of [Bmim]Cl can be eluted from the [Bmim]Cl-loaded resin. Under the same elution conditions, 90.04% of [Bmim]Cl and 52.95% of [HBth]CH₃SO₃H can be eluted from the [Bmim]Cl/[HBth]CH₃SO₃H-loaded resin. This study is expected to be helpful in the ILs recycling and the treatment of water pollution.

Keywords—Adsorption; ion-exchange resin; ionic liquid; cellulosic hydrolysate; desorption

I. INTRODUCTION

Ionic liquids (ILs) have developed wide applications as solvent or catalyst in a range of fields due to their negligible vapor pressure, non-flammability, high thermal stability and tunable solubility. Moreover, the specific properties of ILs can be designed by appropriate modification of the cations or anions [1]. This flexibility has earned them wide applications. Until now, many studies have demonstrated that ILs can be successfully used not only in industrial applications, including Diels-

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B. Preparation of cellulosic hydrolysate

Solution with 2.5 wt% bagasse cellulose in [Bmim]Cl was prepared under vigorous stirring at 100 oC to form a transparent solution, followed by the addition of a small amount of water and acidic IL ([HBth][CH$_3$SO$_3$] or [C$_3$SO$_3$Hmim]HSO$_4$, descending as catalyst). The mixture was stirred at a reaction temperature for a certain time. After reaction, the sample was quenched immediately by adding some of ultrapure water. The supernatant was subjected to dilute for adsorption experiment.

C. Adsorption and desorption experiment

The resin of 732H (1 g) was brought into 25 mL of cellulosic hydrolysate in a 100 mL Erlenmeyer flask. The flasks were then kept in a shaker at 30 °C for a specified time. After adsorption during the predetermined time, the resin was separated and the remaining concentrations of ILs were determined using UV-vis spectrophotometer, after appropriate dilution. The adsorption efficiency was calculated using the following equation:

\[
E(\%) = \frac{(C_0 - C_1)}{C_0} \times 100\%.
\]

Where E(%) represents the adsorption efficiency percentage, $C_0$ and $C_1$ are the concentrations (μg/mL) of ILs before and after adsorption, respectively.

In the static desorption experiments, the IL-loaded resin was mixed with 25 mL of HCl solution in a 100 mL Erlenmeyer flask under agitation at 150 rpm. The released concentration of IL was evaluated by UV-vis spectrophotometer. The desorption efficiency can be described by

\[
D(\%) = \frac{C_2}{(C_0 - C_1)} \times 100\%.
\]

Where D(%) represents the desorption efficiency percentage, $C_2$ is the concentration of ILs in desorption solution (μg/mL), $C_0$ and $C_1$ are the same as described above.

D. Determination of standard curve of IL and TRS

Standard curve of ILs and TRS was established by TU1810 UV-spectrophotometer at maximum absorption wavelength of 210 nm for 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), 211 nm for 1-propyl sulfonic acid-3-methylimidazolium hydrogensulfate ([C$_3$SO$_3$Hmim]HSO$_4$), 252 nm for benzothiazolium methanesulfonate ([HBth][CH$_3$SO$_3$]) and 490 nm for total reducing sugars (TRS) with redistilled water as reference. The TRS was measured using phenol-sulfuric acid method. And the concentration of TRS was calculated based on the standard curve obtained with glucose.

ILs/TRS-water solutions of different concentration were prepared and their absorbance was measured at maximum absorption wavelength, regression equation with favourable linear correlation between absorbance with concentration was arrived as $y=0.0237x+0.0254$,
efficiency reached a plateau beyond 80 min, indicating that adsorption equilibrium was achieved. Because the ion-exchange resin of 732H has almost no adsorption for \([C_3SO_3Hmim]HSO_4\), therefore, the figure of ion-exchange resin of 732H for \([C_3SO_3Hmim]HSO_4\) adsorption was not displayed.

![Figure 4. Effect of adsorption time](image)

**C. Static Desorption**

In this study, the concentration of HCl had an important impact on the desorption process. As shown in Fig. 5, the desorption efficiency increased with increasing the concentration of HCl, thus an aqueous solution of 15% HCl was selected as eluting agent. As a result, 92.05% of \([Bmim]Cl\) can be eluted from the \([Bmim]Cl\)-loaded resin. Under the same elution conditions, 90.04% of \([Bmim]Cl\) and 52.95% of \([HBth]CH_3SO_4\) can be eluted from the \([Bmim]Cl\)-\([HBth]CH_3SO_4\)-loaded resin. The relative low desorption efficiency of \([HBth]CH_3SO_4\) may be attributed as the strong \(\pi-\pi\) interaction between aromatic nucleus of resin with benzothiazolium ring.

![Figure 5. The effect of concentration of HCl on desorption efficiency](image)

**IV. CONCLUSIONS**

Ion-exchange resin was evaluated to determine the adsorption performance for ILs in cellulosic hydrolysates. As a result, the resin of 732H exhibits promising sorption abilities for \([Bmim]Cl\) and \([HBth]CH_3SO_4\), especially for \([HBth]CH_3SO_4\), while no sorption for \([C_3SO_3Hmim]HSO_4\). The result can be due to the stronger \(\pi-\pi\) interaction between aromatic nucleus of resin with benzothiazolium ring than with imidazolium ring. Another primary reason is that \([C_3SO_3Hmim]HSO_4\) possesses a sulfonic acid functional group in its cation. The static desorption experiment of ionic liquids was investigated, the result indicated that 92.05% of \([Bmim]Cl\) can be eluted from the \([Bmim]Cl\)-loaded resin. Under the same elution conditions, 90.04% of \([Bmim]Cl\) and 52.95% of \([HBth]CH_3SO_4\) can be eluted from the \([Bmim]Cl\)-\([HBth]CH_3SO_4\)-loaded resin. This work is expected to be helpful in the ILs recycling and the treatment of water pollution.

**ACKNOWLEDGMENT**

This work was financially supported by the National Scientific Foundation of China (81102344) and 2013 scientific research foundation of Sichuan University for Outstanding Young Scholars.

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