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Sodium hydroxide regeneration of trialkylamine extractant containing inhibitors from corn stover prehydrolyzate by liquid–liquid extraction

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ABSTRACT

Trialkylamine was an effective extractant for the removal of inhibitors from corn stover prehydrolyzate. Ethanol fermentability of the extracted prehydrolyzate was improved significantly. An approach for regeneration and valuable solutes (mainly acetic acid) recovery from such extractant was to back-extract the extractant containing inhibitors with sodium hydroxide. The influences of NaOH concentration, aqueous–organic phase ratio (A/O) on the extractant regeneration were investigated. The results indicated that 17.5 g/l NaOH could remove 100% acetic acid at A/O of 1:1. 175 g/l NaOH at A/O of 1:10 could also reach the same effect. Likewise, the results of 175 g/l NaOH at A/O of 1:1 repeatedly back-extracted the extractant for ten cycles were the same as before. The performance of regenerated extractant on extraction the corn stover prehydrolyzate showed almost no change after reused ten cycles. So NaOH was very suitable to regenerate the extractant containing inhibitors in bioethanol industry.

1. Introduction

The production of lignocellulosic ethanol is well-entrenched in policy and develops quickly because it is a potential substitute for petroleum-based fuels [1,2]. Lignocellulose as feedstock has been focused on because of its renewable nature, abundance and low cost [3]. Ethanol production from lignocellulose mainly involves three steps, pretreatment, enzymatic hydrolysis and ethanol fermentation [4]. In each step, some key problems are gradually being solved [5–12]. For example, Yang et al. [12] realized three-stage enzymatic hydrolysis at high substrate contents (30%) and a short time (30 h), and obtained a hydrolysis yield of 81.4% under the enzyme loading of 30 FPU/g cellulose. However, some questions are also not yet solved. For instance, a series of inhibitors [weak acids (formic acid, acetic acid, levulinic acid, etc.), furan derivatives (furfural, 5-hydroxymethylfurfural, etc.) and phenolics] are inevitably generated during the process of pretreatment. These inhibitors can restrain the following enzymatic hydrolysis and ethanol fermentation [13]. There are two possible solutions, one is to adapt the microbial for fermentation, and another is to detoxify or remove the inhibitors from the prehydrolyzate [14]. A lot of literatures have been written about different detoxification methods to improve the performance of enzymatic hydrolysis and ethanol fermentation, which include physical, chemical, biological and combined methods, such as steam stripping [14], evaporation [13], neutralization [15], overliming [16], ion-exchange [17], electrodialysis [18], membrane extraction/distillation [19,20], dianonofiltration [21], nanofiltration/RO membranes [22], adsorption by activated carbon [23], treatment with microbials [24] or enzyme [25], and so on [26,27]. Trialkylamine extraction was a new method in detoxification of corn stover prehydrolyzate because of its high removal of inhibitors and lossless of sugars [27].

Trialkylamine extractant, composed of trialkylamine, n-octanol and kerosene, is a kind of ion-associated extraction system. When the extractant was used to detoxification, the inhibitors in the aqueous phase transferred to the organic phase, and the organic phase could be regenerated for recycle [28]. The regeneration methods of trialkylamine extractant mainly include four types: temperature swing effect, pH swing effect, the compositions of diluents swing effect and volatile organic alkali swing effect [29–31]. Among these methods, pH swing effect is a simple method to realize the extractant regeneration, but the chemical composition of the regenerated extractant has been changed modestly. If the practical system allows the change of chemical forms, pH swing effect is a good choice to regenerate the extractant. Trialkylamine extractant is widely applied in many areas, such as wastewater

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treatment, separation, purification, and so on. However, the studies of trialkylamine extractant to detoxify lignocellulosic prehydrolyzate and regeneration of trialkylamine extractant in the bioethanol industry are relatively few [27]. In this work, sodium hydroxide was chosen as the regeneration solvent. The effects of NaOH concentration, the A/O on the extractant regeneration were investigated. The extraction capability of NaOH solution and the performance of regenerated extractant on back-extraction of the corn stover prehydrolyzate were also studied. The investigation index was based on the removal of main inhibitor, acetic acid in the organic phase (trialkylamine extractant).

2. Methods

2.1. Reagents

Trialkylamine, n-octanol and kerosene were all of chemical purity. Sodium hydroxide and all the other reagents were of analytical or HPLC grade.

2.2. Detoxification of corn stover prehydrolyzate

Corn stover was obtained from Huhehaote, Inner Mongolia Autonomous Region, China, and was milled and sieved and the fraction between 0.2 and 0.4 mm was used. The pretreatment was performed in a laboratory conventional experimental set-up, which included a glass breaker and an airtight vessel. Corn stover was placed in 1000 ml glass breaker to immerse in 2% (w/v) sulfuric acid solution with a solid–liquid ratio of 1:15 (w/v) at room temperature overnight, and then left to drain off with filtration. The solid residue was milled and kept in a 500 ml airtight vessel at 100 °C of incubator for 12 h to continue prehydrolysis. After that, the prehydrolyzate was collected by filtration; the solid residue was washed three times and the filtrates were added to the prehydrolyzate. The prehydrolyzate was concentrated by BÜCHI rotary evaporator R-200 at 70 °C and 160 mbar until xylose concentration reached approximately 50 g/l for the following study.

10 ml of corn stover prehydrolyzate was placed in 100 ml shaking flask to detoxify by trialkylamine extractant (30% trialkylamine-50% n-octanol-20% kerosene) at A/O of 1:2. Then the flask was shaken at 200 rpm at 25 °C for 60 min to perform extraction [27]. After extraction, the mixture was centrifuged at 5000 rpm for 5 min to separate two phases. The upper organic phase, namely the extractant containing inhibitors was collected by removal of the lower aqueous phase for the next regeneration extraction experiments.

2.3. Back-extraction experiments by NaOH

10 ml of different concentrations of NaOH (10.0, 12.5, 15.0, 17.5, 20.0, and 25.0 g/l) were placed in 100 ml shaking flask to back-extact the extractant containing inhibitors at various A/Os [0.25:1, 0.5:1, 1:1, 2:1, 3:1, 4:1 and 5:1 (v/v)]. The flasks were shaken at 200 rpm and 25 °C for 60 min.

Considering the practical industrial application, higher concentrations of NaOH (100, 125, 150, 175, 200 and 250 g/l) were introduced. The A/O was decreased to 1:10, while the shaking speed, the extraction temperature and time were kept the same as the control experiment.

2.4. Evaluation of the extraction capability of NaOH

In order to evaluate the extraction capability of NaOH, NaOH of ten-fold concentration of its optimum value continuously extracted the extractant containing inhibitors for ten cycles at A/O of 1:1, 200 rpm and 25 °C for 60 min after separation by centrifugation in every cycle.

2.5. Extraction validation of regenerated extractant

The extraction performance of regenerated extractant was studied. After the corn stover prehydrolyzate was extracted with trialkylamine extractant, the extractant containing inhibitors was regenerated with NaOH. Then the regenerated extractant was reused for extraction of the corn stover prehydrolyzate. The operation of extraction and regeneration was circulated ten cycles as previous.

2.6. Analysis

Sugars (cellobiose, glucose, xylose and arabinose), and inhibitors (formic acid, acetic acid, levulinic acid, 5-hydroxymethylfurfural and furfural) were determined by high performance liquid chromatography (HPLC) using an Agilent 1100 system equipped with a refractive index detector. Separations were performed on a Bio-Rad Aminex HPX-87H column (300 × 7.8 mm i.d.) at 55 °C using 0.005 mol/l sulfuric acid as the mobile phase (0.6 ml/min). At least three parallel samples were used in all analyses; data were presented as the mean of the replicates. Relative errors were determined to be within 5% for sugar and ethanol analysis and 10% for inhibitor assay.

Absorbance of the prehydrolyzate with/without trialkylamine extraction was determined with an Amersham Biosciences UV/Visible spectrophotometer. The prehydrolyzate was diluted 100 times for measurement at 280 nm.

3. Results and discussion

3.1. Compositions of corn stover prehydrolyzate before and after extraction

Corn stover prehydrolyzate was conducted with trialkylamine extractant (30% trialkylamine-50% n-octanol-20% kerosene) at A/O of 1:2 on a shaker at 200 rpm and 25 °C for 60 min. The compositions of corn stover prehydrolyzate, aqueous phase and organic phase after extraction are presented in Table 1.

From Table 1, it could be found that the concentrations of sugars (cellobiose, glucose, xylose and arabinose) in the aqueous phase after extraction increased slightly, probably because a small amount of water was extracted into the organic phase, whereas the inhibitors decreased at a different extent. The removal ratios of furfural, acetic acid, formic acid, levulinic acid and 5-hydroxymethylfurfural were 100.0%, 72.7%, 61.3%, 43.9% and 42.9%, respectively. Consequently, trialkylamine extraction could efficiently remove inhibitors and did not lose the sugars [17], which was also the main cause of choosing trialkylamine as extractant.

Absorbance at 280 nm represented the absorbance of furans and lignin degradation products [32]. The absorbance at 280 nm of the extracted prehydrolyzate (0.73) was lower than that of the corn stover prehydrolyzate (1.24) because furans and phenolics were removed partially (phenolics data not shown). Meanwhile, the pH of the extracted prehydrolyzate (4.55) was much higher than that of the corn stover prehydrolyzate (0.59) because acid compounds, especially sulfuric acid were also extracted into the organic phase [29,30]. Therefore, trialkylamine extraction was not only able to remove inhibitors, but also capable of removing sulfuric acid, which could reduce ion strength of the extracted prehydrolyzate. The obtained sulfate could be recovered by some methods for other use.