

## Article

# A New Approach for Economical Pretreatment of Corncobs

Yan Wang <sup>1</sup>, Yanci Hu <sup>2</sup>, Pengfei Qi <sup>3</sup> and Lei Guo <sup>1,4,\*</sup><sup>1</sup> College of Applied Technology, Qingdao University, Qingdao 266061, China; yanwang@qdu.edu.cn<sup>2</sup> Qing Dao ANYIKE Testing Co., Ltd., Qingdao 266061, China; huyanci001@163.com<sup>3</sup> College of Materials and Engineering, Qingdao University, Qingdao 266071, China; pengfei\_q@hotmail.com<sup>4</sup> State Key Laboratory of Safety and Control for Chemicals, SINOPEC Research Institute of Safety Engineering, Qingdao 266071, China

\* Correspondence: xianger001@163.com; Tel.: +86-532-8890-9051

Received: 3 January 2019; Accepted: 28 January 2019; Published: 1 February 2019



**Featured Application:** The research presented in the paper is related to the development of a method aiming at cost-effective pretreatment of corncobs based on the re-use of extremely dilute sulfuric acid as the pretreatment liquid. This method can be applied for corncobs pretreatment in the process of xylose preparation to diminish water and sulfuric acid consumption.

**Abstract:** Huge amounts of waste acid and wastewater are generated during the corncob pretreatment process, which limits chemical utilization of biomass resources to produce value-added chemicals and biofuels. In this work, a new approach, i.e., reuse of the corncob pretreatment liquid, is proposed toward diminishing acid and water consumption. Metal ions and soluble proteins in the pretreatment liquid were analyzed by the inductively coupled plasma atomic emission spectroscopy (ICP-AES) and the Coomassie brilliant blue G250 method, respectively. The results showed that the increment of soluble proteins and total metal ions in solution by three reuse rounds of the pretreatment liquid is nearly identical to that in solution by new added pretreatment liquid. Besides, the surface morphology of the corncob obtained by three reuse rounds of the liquid pretreatment did not exhibit significant difference comparing to that of the corncob acquired by new liquid pretreatment. Further, selection basis of an optimal reuse round of the pretreatment liquid is suggested depending on the effective removal of soluble proteins and metal ions from corncobs. By repeated use of the pretreatment liquid, the consumption of both acid and water during the corncob pretreatment process is expected to be significantly reduced.

**Keywords:** corncob pretreatment; soluble proteins; metal ions; reuse rounds of the pretreatment liquid; acid and water saving

## 1. Introduction

In recent years, shortages of resources and energy are key issues that become more and more significant and have to be confronted in many countries. The development and utilization of biomass resource is known as an effective means to address this issue due to its unique characteristics such as high abundance, superior renewability, and remarkable sustainability [1]. In fact, effective transmission of biomass to value-added chemicals and high energy-density fuels has received considerable attention, which is pivotal for a more sustainable economy and carbon-neutral society [2]. Biomass is a promising renewable energy that can be derived from various sustainable sources, including lignocellulose, lipids, starch, and aquatic plants. Among various biomass resources, corncob is highly valued since it contains large amounts of pentosans and hexoses. In fact, corncob is an important raw material

for producing pentose [3], hydroxymethylfurfural [4], ethanol [5], xylitolp [6], levulinic acid [7], formic acid and acetic acid [8], etc. These products are highly applicable in various fields including food, medicine [9,10], and fine chemicals [11,12]. However, due to production costs and technical restrictions, large majority of corncobs are still incinerated, giving rise to huge waste of resources and severe environmental problems.

For biomass transmission, pretreatment is the most critical processing step, influencing downstream processes [13] such as conditioning of pretreated samples, recovery of coproducts, and wastewater treatment [14]. More importantly, an appropriate pretreatment setp is essential to improve the conversion rate of biomass resources to value-added chemicals and to reduce difficulties on subsequent separation and purification of the final products. Depending on different target products, biomass pretreatment approaches can be various [15]. To date, techniques on effective pretreatment of biomass are well developed, including steam explosion method [16,17], alkali treatment [18,19], supercritical water gasification [20], microbial treatment [21], acid treatment [22], etc. For example, Kim et al. [14] proposed a two-setp corn stover pretreatment method, i.e., hot water pretreatment followed by disk milling, to achieve high sugar yields with low inhibitor concentrations. Narra et al. [18] adopted the mild alkali for rice straw pretreatment. By removing the majority of the lignins while increasing the content of cellulose, the efficiency of enzymatic hydrolysis at high-solid loadings for fermentable sugar production are improved.

Among various pretreatment methods, acid treatment has been widely utilized for corncob pretreatment, especially in industrial production due to its technically mature. During the acid pretreatment process, dilute sulfuric acid and/or nitric acid are usually adopted since they are low-cost and readily available chemicals for industrial applications. It is known that corncob is lignocellulosic material that has a basic composition of cellulose (40~44%), hemicellulose (31~33%), and lignin (16~18%) [23]. In addition to the basic composition, other substances such as salts, proteins, starch and ashes occupy a small portion (less than 10% in total) of the corncob [24]. Depending on where the corncob originates, the proportions of cellulose, hemicellulose, lignin, and other substances in corncobs vary modestly. Narra et al. [25] used dilute nitric acid for corncobs pretreatment, aiming at converting hemicellulose from corncob to fermentable sugars for bio-methane and bio-ethanol production. Based on the optimized conditions, corncobs were processed with nitric acid concentration of 2.0 vol.% at 121 °C and a 1:5 solid-to-liquid ratio, yielding sugar concentration as high as 110.12 mg·mL<sup>-1</sup>. As an alternative, dilute sulfuric acid was also used as pretreatment solution in Narra's work. By comparison, both acids yield almost the same sugar concentrations at identical operation conditions.

In the process of xylose preparation, corncob raw materials have to be pretreated in order to remove metal ions and soluble proteins that are not conducive to the separation and purification of the xylose product from corncobs [26]. However, studies on pretreatment of corncob raw material for effective eliminating soluble proteins and metal ions have rarely been reported. In our previous study [26], we suggested using an extremely dilute sulfuric acid solution as pretreatment liquid for processing corncob raw material. By exploiting optimum process conditions, the removal rate of soluble proteins and metal ions attained to 97.0% and 94.3%, respectively [26]. Interestingly, as the basic composition of the corncob, the contents of cellulose, hemicellulose and lignin after pretreatment exhibit negligible variations. We believe that this is attributed to the extremely low concentrations of sulfuric acid (0.1 wt.%) utilized for corncob pretreatment under comparatively moderate operating conditions, i.e., a 100 °C processing temperature in combination with an atmospheric pressure.

Despite the afore-mentioned advantages, the acid treatment method is constrained since large amounts of waste acid and wastewater have been produced. The wastewater can be discharged only if it meets relevant discharge standards after treatment; meanwhile, the production efficiency is reduced and the production cost is increased. In industrial corncob pretreatment, the ratio between the mass of the corncob to the volume of the dilute acid solution is generally in the range of 1:10 to 1:5. However, a huge amount of waste acid are generated after pretreatment, which results in extra waste disposal processes. Although the amount of sulfuric acid and water utilized during corncob pretreatment has

been decreasing through a variety of means, reducing the consumption of both acid and water at an order of magnitude level is still an ongoing problem.

In this paper, a new process for economic pretreatment of corncob by repeated using extremely dilute sulfuric acid as the pretreatment liquid is proposed. To evaluate the effect of corncob pretreatment, metal ions and soluble proteins in solution are analyzed respectively for different re-use rounds of the pretreatment liquid. In addition, basis for the selection of an optimal reuse round of the pretreatment liquid are suggested. To the best of authors' knowledge, no previous published work was found in which extremely dilute sulfuric acid as the pretreatment liquid has been reused on corncob pretreatment. The methodological approach presented in this study aims to provide the industrialists and researchers a guideline for design of a cost-effective pretreatment process on corncob conversion with significantly reduced water and sulfuric acid consumption.

## 2. Materials and Method

### 2.1. Materials

Corncoobs (120-mesh) were provided by Zhenhua Corncob Processing Co., Ltd. (Liaocheng, Shandong, China). Sulfuric acid (98 wt.%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The deionized water was self-made in laboratory with the conductivity of  $1.0 \times 10^{-4}$  S/m.

### 2.2. Analytical Method

#### 2.2.1. Analysis of the Soluble Protein

The Coomassie brilliant blue G-250 method [27] was employed to determine the soluble protein content of the solution by using a visible spectrophotometer (V-5100B, Shanghai Yuanyin Instrument Co., Ltd., Shanghai, China). The detection wavelength was 595 nm.

#### 2.2.2. Analysis of the Metal Ions

The samples were subjected to elemental analysis using inductively coupled plasma emission spectrometry (ICP-6300, Thermo Scientific Co., Ltd., Waltham, MA, USA) at a power of 1.20 kW and a plasma flow rate of 15.0 L/min.

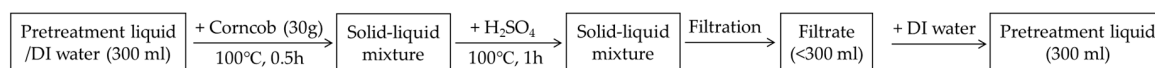
#### 2.2.3. Analysis of Corncob Surface Morphology

SEM images of the corncoobs surface morphology were analyzed by a scanning electron microscope S-3000N (Hitachi Co., Ltd., Tokyo, Japan) at an accelerating voltage of 10 kV. Corncob samples were previously sputter-coated with a uniform palladium layer (<10 nm) by MC1000 (Hitachi Co., Ltd., Tokyo, Japan) under a Vacuum (7.0 Pa) to avoid charging effects.

### 2.3. Experimental Method

The experiments were carried out by adding 30 g corncob raw material and 300 mL deionized (DI) water (or a mixture of pretreatment liquid and deionized water) to a 500 mL three-necked flask. The reaction was conducted by placing the flask to an oil bath heater (HH-WO, Kenuo Instrument Co., Ltd., Tianjin, China) and stirring with a mechanical stirrer (MYP2011-100, Meiyongpu Instrument Co., Ltd., Shanghai, China) while maintaining the operation temperature of 100 °C for 0.5 h to remove soluble proteins from the corncob. Afterward, the 98 wt.% sulfuric acid was added into the solid-liquid mixture to adjust the mass fraction of the sulfuric acid to 0.1% (equivalent to a molarity of  $0.01 \text{ mol} \cdot \text{L}^{-1}$ ), and the reaction was continued at 100 °C for another 1 h to remove metal ions from the corncob. Then the solid-liquid mixtures was filtered and the filtrate was collected. The afore-mentioned experimental process is referred to as the first-round use of the pretreatment liquid (Figure 1). Later, the collected filtrate was further used for corncob pretreatment by adding DI water into the filtrate until

300 mL and another new 30 g corncob raw material while maintaining at 100 °C for 0.5 h. Followed by the concentrated sulfuric acid was added to the solid-liquid mixtures and processed for 1 h. After the reaction was completed, the filtrate was collected. By adding DI water to the filtrate until it reached 300 mL, the pretreatment liquid is thus recovered. This is referred to as the second-round use of the pretreatment liquid. Based on the above experimental procedure, the pretreatment liquid can be reused several times while still guaranteeing a high removal rate of metal ions and soluble proteins from corncobs.



**Figure 1.** Scheme on the experimental process round of the pretreatment liquid applied for corncob pretreatment.

### 3. Results and Discussion

Acid pretreatment of corncobs produce large amounts of waste acid and wastewater. Aiming at this problem, we reused the pretreatment liquid three rounds for corncobs pretreatment. The effect on the removal of metal ions and soluble proteins in the corncob was examined. Due to relatively high contents of  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Na^+$  in corncobs, these four ions were used as the objective metal ions.

#### 3.1. Effect of Reuse of Pretreatment Solution on Soluble Protein Removal in Corncob

##### 3.1.1. Effect of pH Change of the Pretreatment Solution on Soluble Protein Removal in Corncob

The concentration of the soluble protein and the increment of soluble protein in solution after pretreatment of corncobs are presented in Table 1. The corncob was primarily reacted with the deionized water at 100 °C for 0.5 h in order to better remove the soluble proteins from the corncob. However, after adjusting the mass fraction of sulfuric acid solution to 0.1% and continuing the reaction for 1 h, it can be seen from Table 1 that the obtained pretreatment liquid had a pH value of 3.1. After the first reuse round of the pretreatment liquid, the increment of soluble proteins in the pretreatment liquid was 67.2 mg, which exhibits a very small difference as compared to the increment of soluble proteins in the solution after pretreatment of the corncob with the new added pretreatment liquid (68.4 mg). With the pretreatment liquid being reused continuously, the resulting solutions have pH values in the range of 3.1~3.2. No significant differences were found for the increment of soluble proteins in different reuse rounds (from the first to the third reuse round) of the pretreatment liquid comparing to the increment of the soluble proteins in the solution after corncob pretreatment with the new added liquid, indicating that the pretreatment liquid with a pH value of 3.1~3.2 exhibits nearly equivalent effect on removing the soluble proteins from corncob as compared to the newly added liquid.

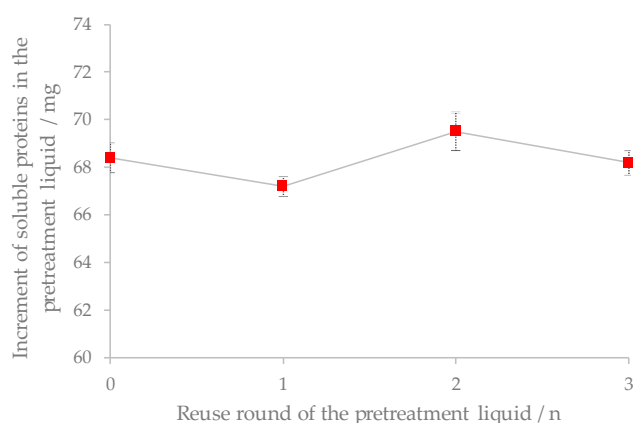
**Table 1.** Concentration increment of soluble protein in solution after corncobs being pretreated.

| Reuse of Pretreatment Liquid (n) | Volume of Previous Used Liquid (mL) | Volume of Deionized Water (mL) | Solution pH after Pretreatment | Concentration of the Soluble Protein ( $mg \cdot L^{-1}$ ) | Increment of the Soluble Proteins (mg) |
|----------------------------------|-------------------------------------|--------------------------------|--------------------------------|--|--|
| 0                                | 0                                   | 300                            | 3.1                            | 228  | 68.4                                   |
| 1                                | 225                                 | 75                             | 3.2                            | 395  | 67.2                                   |
| 2                                | 228                                 | 72                             | 3.1                            | 532  | 69.5                                   |
| 3                                | 226                                 | 74                             | 3.1                            | 628  | 68.2                                   |

##### 3.1.2. Effect of Reuse Round of Pretreatment Liquid on Soluble Protein Removal in Corncob

Figure 2 shows that the increments of soluble proteins in the solution for three reuse rounds of the pretreatment liquid are in negligible difference comparing to the increment of the soluble proteins in the solution after pretreatment of the corncob with the new added liquid. Therefore,

the corncob pretreatment liquid can be continuously reused for effectively removing soluble proteins from the corncob.



**Figure 2.** Increment of the soluble proteins in pretreatment liquid for different reuse round of the pretreatment liquid. The error bars show the standard error of the three mean values from soluble protein measurements.

Note that as long as the increment of soluble proteins in the pretreatment liquid was significantly reduced and/or the soluble proteins in the pretreatment liquid was saturated, the pretreatment liquid was no longer applicable. At this point, we believe that the pretreatment liquid has attained a threshold processing round with respect to effective removal of soluble proteins in the corncob.

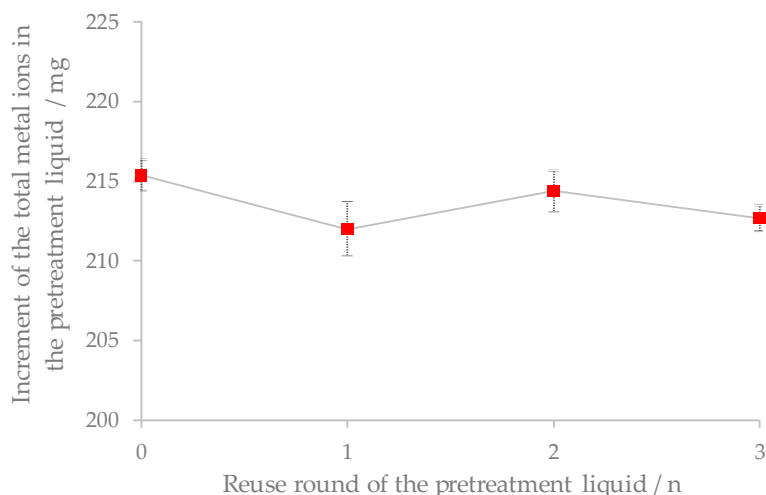
### 3.2. Effect of Reuse of Pretreatment Liquid on Removal of Metal Ions in Corncob

The concentration of metal ions as well as the increment of metal ions in the solution after pretreatment of corncobs are presented in Table 2. It can be seen that the concentrations of  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Na^+$  in solution increase gradually as the reuse round of the pretreatment liquid increases. Meanwhile, the increment of  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Na^+$  in the solution after repeated use of the pretreatment liquid exhibits slight difference comparing to the increment in the solution after pretreatment of the corncob with the new added pretreatment liquid. In Figure 3, the increment of total amount of metal ions in the solution drops only a bit after the pretreatment liquid being reused for three rounds. This negligible drops of the amount of total metal ions found from the pretreatment liquid being reused for three rounds ( $n = 3$ ) as compared to those in the pretreatment liquid only after first use ( $n = 0$ ) can ensure the reuse of the pretreatment liquid for effectively removing metal ions from the corncob.

Note that as long as the increment of metal ions in the pretreatment liquid was significantly reduced and/or the concentration of metal ions reached saturation, the pretreatment liquid were considered no longer usable. At this point, we believe that the pretreatment liquid has attained a threshold processing round with respect to effective removal of metal ions in the corncob.

**Table 2.** Concentration of metal ions and the increment of metal ions in pretreatment solution after corncobs pretreatment.

| Reuse Times of the Pretreatment Liquid/(n) | Concentration of Metal Ions after Pretreatment/(mg·L <sup>-1</sup> ) |                  |                  |                 |              | Increment of Metal Ions after Pretreatment/(mg) |                  |                  |                 |              |
|--|--|------------------|------------------|-----------------|--------------|---|------------------|------------------|-----------------|--------------|
|  | K <sup>+</sup>   | Ca <sup>2+</sup> | Mg <sup>2+</sup> | Na <sup>+</sup> | Total Amount | K <sup>+</sup>                                  | Ca <sup>2+</sup> | Mg <sup>2+</sup> | Na <sup>+</sup> | Total Amount |
| 0  | 638.3  | 59.3             | 16.9             | 3.2             | 717.7        | 191.5   | 17.8             | 5.1              | 1.0             | 215.4        |
| 1  | 1107.6   | 102.2            | 29.1             | 6.0             | 1244.9       | 188.7   | 17.3             | 4.9              | 1.1             | 212.0        |
| 2  | 1477.1   | 136.7            | 39.1             | 7.7             | 1660.6       | 190.6   | 17.7             | 5.1              | 1.0             | 214.4        |
| 3  | 1743.6   | 161.2            | 46.2             | 9.1             | 1960.1       | 189.2   | 17.5             | 5.0              | 1.0             | 212.7        |



**Figure 3.** Increment of total metal ions in the pretreatment liquid for different reuse round of the pretreatment liquid. The error bars show the standard error of the three mean values from total metal ions measurements.

### 3.3. Selection of Reuse Times of the Corncob Pretreatment Liquid

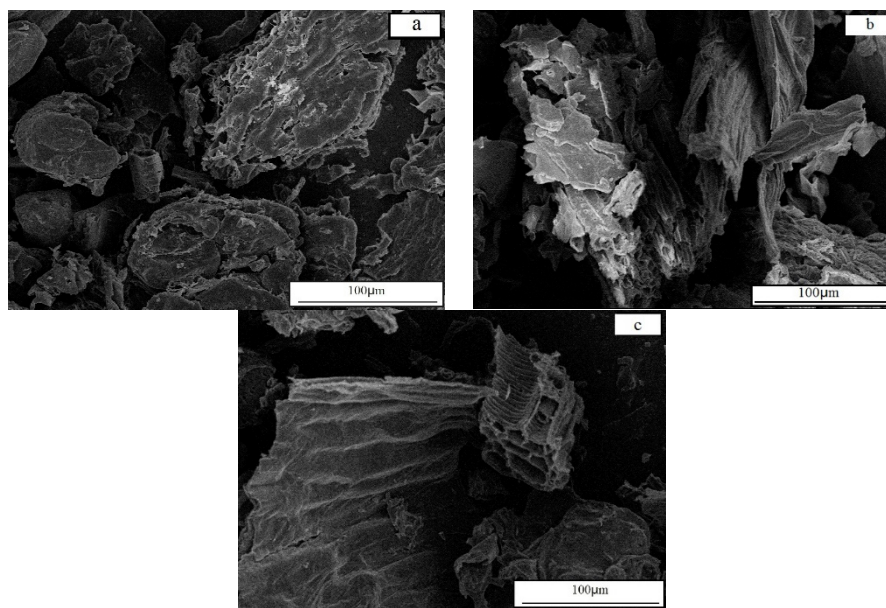
As discussed in Sections 3.1.2 and 3.2, the reuse times of the corncob pretreatment liquid depends significantly on the removal effects of soluble proteins and metal ions in the corncob. That is, an optimal reuse times of the pretreatment liquid is determined by the threshold processing times with respect to effective removal of soluble proteins, only if there was no significant change of the increment of metal ions and/or the metal ions were not saturated in the pretreatment liquid. Likewise, an optimal reuse times of the pretreatment liquid is determined by the threshold processing round with respect to effective removal of metal ions, only if there was no significant change of the increment of soluble proteins and/or the soluble proteins were not saturated in the pretreatment liquid.

Therefore, the number of reuses of the corncob pretreatment liquid can be selected by the combination of removal effects of both soluble protein and metal ions in the corncob.

### 3.4. Morphology Comparison of the Corncob after Pretreatment Liquid and New Liquid Pretreatment

The surface morphology of the raw corncob and the corncob pretreated after three reuse rounds of the pretreatment liquid as well as the corncob pretreated by the new added pretreatment liquid are compared, as shown in Figure 4a–c, respectively. It can be seen that both of the surface morphologies of the corncob pretreated by three reuse rounds of the pretreatment liquid and the corncob pretreated by new pretreatment liquid are smoother and more porous than that of the corncob raw material. The comparative smooth surface of the corncob after pretreatment (Figure 4b,c) may be attributed to the absence of the impurities deposited on the surface of the corncob. Besides, the surface morphology of the corncob obtained after three reuse rounds of the pretreatment liquid (Figure 4b) exhibits no significant difference comparing to the surface morphology of the corncob pretreated by the new pretreatment liquid (Figure 4c), as both have regular and compact surface textures.





**Figure 4.** Comparison of surface morphology for (a) untreated corncobs; (b) corncobs pretreated by the pretreatment liquid for three reuse rounds and; (c) corncobs pretreated by the new added pretreatment liquid. SEM images of (a,c) are taken from our previously published work [26].

#### 4. Conclusions

In this work, a new technology for economic pretreating the corncobs via reusing the pretreatment liquid was proposed. By analyzing the soluble proteins in the pretreated liquid, it was found that the pretreatment liquid with a pH value of 3.1~3.2 exhibits nearly equivalent effect on removing the soluble proteins from corncob as compared to the newly added liquid. The increments of soluble proteins in the solution for three reuse rounds of the pretreatment liquid are in negligible difference comparing to the increment of the soluble proteins in the solution after pretreatment of the corncob with the new added liquid, demonstrating that the pretreatment liquid can be reused for effectively removing soluble proteins from the corncob. From analysis of metal ions in the pretreatment liquid, the increment of total amount of metal ions in the solution drops only a little after the pretreatment liquid is reused for three rounds. The negligible drops of the amount of total metal ions found in the pretreatment liquid reused for three rounds comparing to those only after once use can ensure the reuse of the pretreatment liquid for effectively removing metal ions from the corncob. Furthermore, the surface morphology of the corncob obtained after three reuse rounds of the pretreatment liquid exhibits no significant difference compared to the surface morphology of the corncob pretreated by the new pretreatment liquid, with smoother and more porous surfaces than that of the corncob raw material. The number of reuses of the corncob pretreatment liquid can be determined by the combination of removal effects of both soluble protein and metal ions in the corncob. The proposed process provides a guideline for diminishing both acid and water consumption, allowing for the economic and environmentally friendly pretreatment of corncobs with reduced pollutant emission.

**Author Contributions:** Funding acquisition, Y.W.; Conceptualization Y.W. and L.G.; Methodology, Y.W., L.G. and Y.H.; Data acquisition, Y.H.; Investigation, Y.W., P.Q. and L.G.; Original draft writing, Y.W. and L.G.; Review and editing, Y.W., P.Q. and L.G.; supervision, L.G.

**Funding:** This research was supported by the National Nature Science Fund Program of China (Project number 21808116).

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Sudarsanam, P.; Zhong, R.; Van den Bosch, S.; Coman, S.M.; Parvulescu, V.I.; Sels, B.F. Functionalised Heterogeneous Catalysts for Sustainable Biomass Valorization. *Chem. Soc. Rev.* **2018**, *47*, 8349–8402. [[CrossRef](#)] [[PubMed](#)]
2. Ambursa, M.M.; Ali, T.H.; Lee, H.V.; Sudarsanam, P.; Bhargava, S.K.; AbdHamid, S.B. Hydrodeoxygenation of Dibenzofuran to Bicyclic Hydrocarbons Using Bimetallic Cu–Ni Catalysts Supported on Metal Oxides. *Fuel* **2016**, *180*, 767–776. [[CrossRef](#)]
3. Yu, N.; Zhu, Z.Y.; Liu, Y.; Zhang, J.Y.; Zhang, Y.M. Chromatographic Analysis and Preparation of l-arabinose from Corn cob by Acid Hydrolysis. *Ind. Crops Prod.* **2017**, *95*, 163–169. [[CrossRef](#)]
4. Rout, P.K.; Nannaware, A.D.; Prakash, O.; Kalra, A.; Rajasekharan, R. Synthesis of Hydroxymethylfurfural from Cellulose using Green Processes: A Promising Biochemical and Biofuel Feedstock. *Chem. Eng. Sci.* **2016**, *142*, 318–346. [[CrossRef](#)]
5. Meena, S.; Navatha, S.; Devi Prabhavathi, B.L.A.; Prasad, R.B.N.; Pandey, A.; Sukumaran, R.K. Evaluation of Amberlyst15 for Hydrolysis of Alkali Pretreated Rice Straw and Fermentation to Ethanol. *Biochem. Eng. J.* **2015**, *102*, 149–165. [[CrossRef](#)]
6. Mardawati, E.; Andoyo, R.; Syukra, K.A.; Kresnowati, M.; Bindar, Y. Production of Xylitol from Corn Cob Hydrolysate through Acid and Enzymatic Hydrolysis by Yeast. *Earth Environ. Sci.* **2018**, *141*, 12–19. [[CrossRef](#)]
7. Joshi, S.S.; Zodge, A.D.; Pandare, K.V.; Kulkarni, B. Efficient Conversion of Cellulose to Levulinic Acid by Hydrothermal Treatment Using Zirconium Dioxide as a Recyclable Solid Acid Catalyst. *Ind. Eng. Chem. Res.* **2014**, *53*, 18796–18805. [[CrossRef](#)]
8. Lu, T.; Hou, Y.C.; Wu, W.Z.; Niu, M.G.; Wang, Y.P. Formic Acid and Acetic Acid Production from Corn Cob by Catalytic Oxidation Using O<sub>2</sub>. *Fuel Process. Technol.* **2018**, *171*, 133–139. [[CrossRef](#)]
9. Li, X.; Wang, Y.; Han, D.; Zhang, W.; Zhang, Z.; Ye, X.; Tian, L.; Dong, Y.; Zhu, Q.; Chen, Y. Correlation of Hepatitis B Surface Antigen Level with Response to Telbivudine in Naive Patients with Chronic Hepatitis B. *Hepatol. Res.* **2014**, *44*, 187–193. [[CrossRef](#)]
10. Preuss, H.G.; Echard, B.; Bagchi, D.; Stohs, S. Inhibition by Natural Dietary Substances of Gastrointestinal Absorption of Starch and Sucrose in Rats and Pigs: 1. Acute Studies. *Int. J. Med. Sci.* **2007**, *4*, 196–202. [[CrossRef](#)]
11. El-Faragy, A.F.; Ghoniem, A.A. Synthesis of some New C-Nucleosides from L-Arabinose and D-Glucose. *ARKIVOC* **2008**, *13*, 278–285.
12. Melero, J.A.; Morales, G.; Iglesias, J.; Paniagua, M.; Hernández, B.; Penedo, S. Efficient Conversion of Levulinic Acid into Alkyl Levulinates Catalyzed by Sulfonic Mesostructured Silicas. *Appl. Catal. A* **2013**, *466*, 116–122. [[CrossRef](#)]
13. Kumar, D.; Murthy, G.S. Impact of Pretreatment and Downstream Processing Technologies on Economics and Energy in Cellulosic Ethanol Production. *Biotechnol. Biofuels* **2011**, *4*, 27–46. [[PubMed](#)]
14. Kim, S.M.; Dien, B.S.; Tumbleson, M.E.; Rausch, K.D.; Singh, V. Improvement of Sugar Yields from Corn Stover Using Sequential Hot Water Pretreatment and Disk Milling. *Bioresour. Technol.* **2016**, *216*, 706–713. [[CrossRef](#)] [[PubMed](#)]
15. Hendriks, A.T.W.M.; Zeeman, G. Pretreatments to Enhance the Digestibility of Lignocellulosic Biomass. *Bioresour. Technol.* **2009**, *100*, 10–18. [[CrossRef](#)] [[PubMed](#)]
16. Yue, Z.B.; Liu, R.H.; Yu, H.Q.; Chen, H.Z.; Yu, B.; Harada, H.; Li, Y.Y. Enhanced Anaerobic Ruminal Degradation of Bulrush through Steam Explosion Pretreatment. *Ind. Eng. Chem. Res.* **2008**, *47*, 5899–5905. [[CrossRef](#)]
17. Keshav, P.K.; Naseeruddin, S.; Rao, L.V. Improved Enzymatic Saccharification of Steam Exploded Cotton Stalk Using Alkaline Extraction and Fermentation of Cellulosic Sugars into Ethanol. *Bioresour. Technol.* **2016**, *214*, 363–370. [[CrossRef](#)]
18. Narra, M.; Balasubramanian, V.; James, J.P. Enhanced Enzymatic Hydrolysis of Mild Alkali Pre-Treated Rice Straw at High-Solid Loadings Using in-House Cellulases in a Bench Scale System. *Bioprocess. Biosyst. Eng.* **2016**, *39*, 993–1003. [[CrossRef](#)]
19. Qin, W.J.; Chen, Y.F.; Zhao, H.Y.; Wang, R.S.; Xiao, D.G. Optimization of Pretreatment Conditions for Corn Cob with Alkali Liquor. *Trans. Chin. Soc. Agric. Eng.* **2010**, *26*, 248–253.



20. Lu, Y.J.; Guo, L.J.; Zhang, X.M.; Ji, C.M. Hydrogen Production by Supercritical Water Gasification of Biomass: Explore the Way to Maximum Hydrogen Yield and High Carbon Gasification Efficiency. *Int. J. Hydrog. Energy* **2012**, *37*, 3177–3185. [[CrossRef](#)]
21. Shi, J.; Sharma-Shivappa, R.R.; Chinn, M.; Howell, N. Effect of Microbial Pretreatment on Enzymatic Hydrolysis and Fermentation of Cotton Stalks for Ethanol Production. *Biomass Bioenergy* **2009**, *33*, 88–96. [[CrossRef](#)]
22. Rafiqul, I.S.M.; Sakinah, A.M.M.; Karim, M.R. Production of Xylose from Meranti Wood Sawdust by Dilute Acid Hydrolysis. *Appl. Biochem. Biotechnol.* **2014**, *174*, 542–555. [[CrossRef](#)] [[PubMed](#)]
23. Wang, L.; Yang, M.; Fan, X.G.; Zhu, X.T.; Xu, T.; Yuan, Q.P. An Environmentally Friendly and Efficient Method for Xylitol Bioconversion with High Temperature Steaming Corncob Hydrolysate by Adapted *Candida Tropicalis*. *Process Biochem.* **2011**, *46*, 1619–1626. [[CrossRef](#)]
24. Pointner, M.; Kuttner, P.; Obrlik, T.; Jäger, A.; Kahr, H. Composition of Corncobs as a Substrate for Fermentation of Biofuels. *Agron. Res.* **2014**, *12*, 391–396.
25. Narra, M.; Macwan, K.; Vyas, B.; Harijan, M.R.; Shah, D.; Balasubramanian, V.; Prajapati, A. A Bio-refinery Concept for Production of Bio-methane and Bio-ethanol from Nitric Acid Pre-treated Corncob and Recovery of a High Value Fuel from a Waste Stream. *Renew. Energy* **2018**, *127*, 1–10. [[CrossRef](#)]
26. Guo, L.; You, W.N.; Zhao, X.; Hu, Y.D.; Wu, L.Y. Pretreatment Technology of Desalination and Deproteinization of Corn Cobs. *Chem. Ind. Eng. Prog.* **2017**, *36*, 1927–1932.
27. Deng, L.L.; Pan, X.Q.; Sheng, J.P.; Shen, L. Optimization of experimental conditions for the determination of water-soluble protein in apple pulp using coomassie brilliant blue method. *Food Sci.* **2009**, *33*, 185–189.



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).