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Research Article

Fermented Corn Stalk for Biosorption of Copper(II) from Aqueous Solution

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Corn stalk is the amplest and inexpensive organic material in Heilongjiang province, China. This resource is vicious, causing pollution of the environment. In this present study, an adsorbent is prepared by corn stalk fermentation with *Aspergillus niger*. The fermentative effects of water content ratio, initial pH medium, temperature, and time were addressed. The analysis of factors and orthogonal experiments revealed that the optimum conditions of producing cellulose were solid-liquid ratio of 1 : 5, temperature 28°C, initial pH, and 72 hours. The modification mechanism was investigated by using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The biosorption capacity of fermented corn stalk was better than that of raw corn stalk under identical conditions, and this improvement can be ascribed to the enzyme system secretion by *A. niger* under changing the surface properties of the raw corn stalk. Some of the hydroxyl and carboxyl groups are bounded by cellulose which became free hydroxyl and carboxyl groups with a high ability after adsorption of heavy metals.

1. Introduction

Heavy metal discharge causes serious environmental problem due to non-biodegradability. But these metals accumulate in living tissues. Copper is widely being used in industrial applications, but its removal and recovery from wastewater is necessary for protection of the environment as well as human health [1–3]. Several methods, such as chemical precipitation, coagulation, electrochemical treatment, membrane separation, solvent extraction, and ion exchange are available for the treatment of metal-bearing effluents and were applied to reduce the copper concentration of wastewater [4–7]. However, these methods have limitations, including secondary pollution, high-cost and high-energy input with requirement of large quantities of chemical reagents, and poor treatment efficiency at low metal concentration [8]. The alternative biosorption methods are exhibited to overcome these drawbacks.

Many studies have focused on the use of agricultural and food industry waste, such as pine cones, shells and powder [9], almond shells [10], tomato waste [11], and *Acidosasa edulis* shoot shells [12] but biosorbents remove heavy metals from polluted water. Agricultural discard, especially corn stalk (corn is a major crop in Heilongjiang province, providing grain reserves, feed, and industrial raw materials) is an important part of agricultural straw in Heilongjiang province. Another abundant straw waste, rice, was chemically modified and studied as a biosorbent by Vafakhah et al. [13]. A mixture of corn stalk and tomato waste was oxidized with nitric acid, used to investigate the adsorption of copper(II) ions. Wang etal. [14] prepared corn stalk-based adsorbents that were modified by Cu (0)-mediated reversible-deactivation radical polymerization (Cu (0)-mediated RDRP) and applied to remove metal ions Hg(II). However, chemical treatment (acid or alkali) may create secondary microbiological modification for friendly environment [15]. *Aspergillus niger* can endure and adapt to various environmental conditions. Functional groups on the cell wall of biomaterials such as corn stalk, include hydroxyl, carboxyl, carbonyl, and amine with a high affinity to form metal complexes [16]. In this study, we have prepared corn stalk fermentation by using *A. niger* and have tested the properties of this material as a biosorbent. Although, there are some reports related to chemical modification of corn stalk, to the best of our knowledge, there have been no published work about the biological treatment for this material. This study determined the optimal culturing conditions for the modification of corn stalk by *A. niger* and compared biosorption capacity of the fermented corn stalk (FCS) with the untreated corn stalk. Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were used to probe the properties of the sample.

2. Materials and Methods

2.1. Microorganism. Aspergillus niger was isolated from nature, the spore suspension was prepared by washing the aerial mycelium with water, and concentration was adjusted up to 10^6 cfu/ml. The spore concentration of the final suspensions was determined by counting in hemocytometer.

2.2. Culture Medium. The corn stalk was washed with distilled water, crushed with a grinder (FW100, Tianjin Theis), and sieved with a standard way to obtain powder with a particle diameter of 0.3 mm. Then, the powder was dried in an electrically heated blast dry box to a constant weight.

2.3. Optimal Culture Conditions

2.3.1. Effect of Solid-Liquid Ratio. In this case, to determine the effect of the solid-liquid ratio, the spore suspension was added into the corn stalk medium at a solid-liquid ratio, ranged from 1 : 1 to 1 : 7 at 28 °C for 72 h. It gives the clear effect of such ratios.

2.3.2. Effect of Initial pH. In order to figure out the effect of the initial pH, spore suspension was added into the corn stalk medium with the optimal solid-liquid ratio at different pH values of 4.0, 4.4, 5.0, 5.4, 6.0, and 6.4 at 28 °C for 72 h. The pH values were controlled by the addition of citric acid buffer solution (0.2 M).

2.3.3. Effect of Temperature. Effect of temperature describes the optimal temperature, and spore suspension was added into the corn stalk medium with an optimal solid-liquid ratio and pH under different temperatures (25 °C, 28 °C, 30 °C, 32 °C, and 34 °C) for 72 h.

2.3.4. Effect of Time. In order to find out the effect of the fermentation time, spore suspension was added into the corn stalk medium with the best optimal solid-liquid ratio, pH, and temperature for different times (48 h, 72 h, 96 h, 128 h, and 168 h), respectively.

2.3.5. Effect of Excess Carbon and Nitrogen Source. In this case, we have focused on the effects of excess carbon and nitrogen sources after adding into the culture medium.

2.4. Biosorption Experiment. We evaluated the biosorption of the prepared materials, and 0.15 g dry biosorbent material was put into 100 mL of $CuSO_4{\cdot}5H_2O$ solution with an initial Cu^{2+} concentration of 20 mg/L. The flasks were shaken at 30°C with 150 rpm for 30 minutes. The Cu^{2+} solution was filtered through a membrane with a pore diameter of 0.45 μm, and analyzed by inductively coupled plasma mass spectrometry to determine the concentrations of the Cu^{2+} before and after biosorption.

2.5. Regeneration Studies of Fermented Corn Stalk. To evaluate the reusability, regeneration of the spent adsorbent was studied. At first, 0.1 g of the adsorbent was loaded by 100 mL of 20 mg/L Cu(II) solution. After attaining equilibrium, the exhausted biosorbent was separated from the solution through a membrane with a pore diameter of 0.45 μm. Subsequently, metal ions were eluted by using 0.1 M HCl. The regeneration of the biosorbent was sequentially operated three times in this way. All the samples were chemically analyzed for metal determination.

2.6. Biosorption of a Binary Metal Solution. Three pairs of competitive biosorption experiments for Cu^{2+} and Pb^{2+}, Cu^{2+} and Ca^{2+}, and Cu^{2+} and Cd^{2+} ions were performed using the biosorbent. The initial concentration of all the heavy metals was 20 mg/L, and the biosorbent dosage was 0.15 g. The metals and biosorbent were shaken together at 30°C for 30 minutes.

2.7. Biosorbents Characterization. After being dried to a constant weight, the modified corn stalk and raw corn stalk samples were screened by Fourier transform infrared spectroscopy (FTIR 1730 model, PerkinElmer, Inc.,) via KBR tablet method. The scanning electron microscopy (SEM SU8018, Japan) was employed to under seek the morphology of the two kinds of biosorbents. But the dried biosorbent was coated with gold for better contrast.

3. Results and Discussion

3.1. Effect of Solid-Liquid Ratio. In solid fermentation culturing, the corn stalk serves as the culture medium because it has almost no water. The requirement for additional water was assayed by changing the solid-liquid ratio. Figure 1 displays the results of testing the effect of different solid-liquid ratios of corn stalk on biological modification. The solid-liquid ratio of 1 : 5, yielded the highest biosorption rate. An appropriate amount of water allows nutrients for absorption in the culture medium, but if there is little water, *Aspergillus niger* cannot absorb nutrients, and growth will be inhibited. If there is too much water, there may be an insufficient concentration of oxygen in the culture medium, and it limits the fermentation.

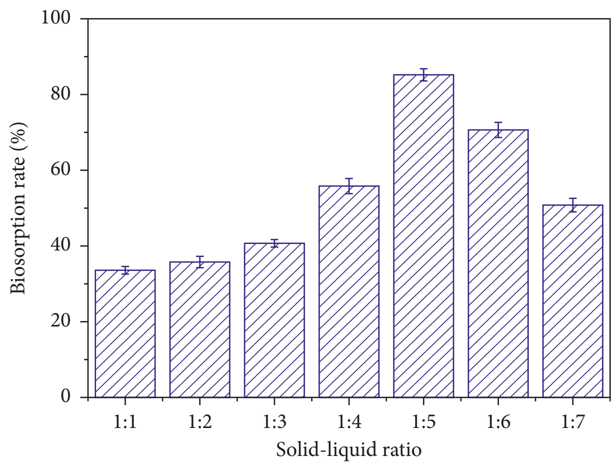

Figure 1: Effect of the solid-liquid ratio on biological modification.

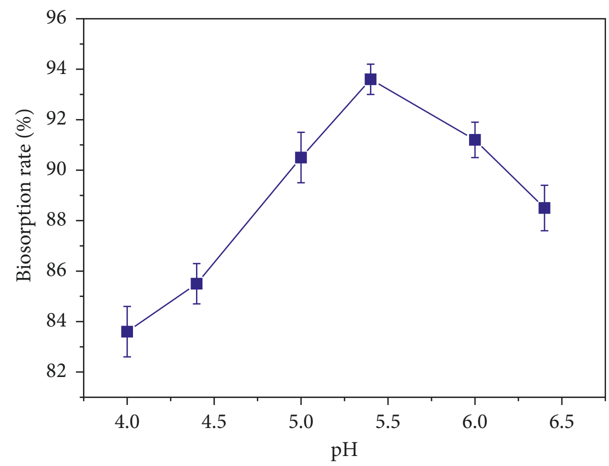

Figure 2: Effect of pH values on biological modification.

3.2. Effect of Initial pH. Figure 2 exhibits the effect of different pH values of the culture medium on biological modification. Citric acid buffer solution was used to control the pH value of the culture medium throughout the solid fermentation process. The pH value varies from 4 to 6.5 against biosorption rate (%). The corn stalk was better modified when the pH value was in the range of 5.0 to 6.0. But the best biosorption was considered at pH = 5.4 in our work. It should be noted, without use of the citric acid buffer solution, the pH values change greatly. This phenomenon suggests that production occurs during the modification, resulting the decreasing pH value of the culture medium. Hence, the enzyme activity is suppressed by the lower pH and the biosorption rate [17].

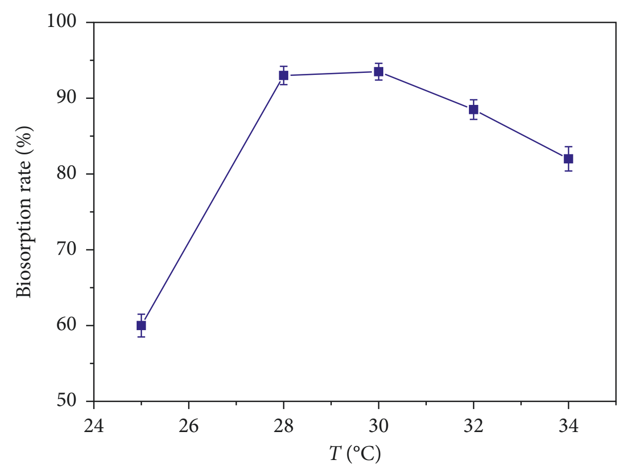

Figure 3: Effect of temperature on biological modification.

3.3. Effect of Temperature. Figure 3 displays the effect of culture temperature on biological modification. The results show that the culture temperature has a great influence on the solid fermentation process. When the culture temperature is too low, *Aspergillus niger* hyphae grow slowly, resulting in less cellulose and poor modification. When the culture temperature is too high, *Aspergillus niger* hyphae grow faster but microbial cell function decreases due to the high temperature, resulting in less cellulose and poor biosorption [18]. The best modification was observed clearly after controlling the culture temperature at 28–30°C.

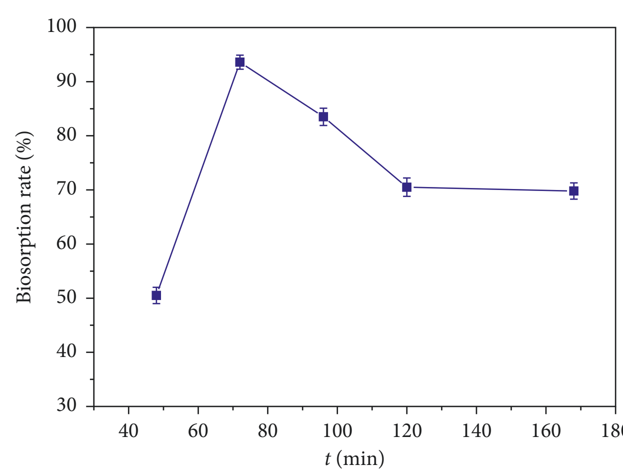

Figure 4: Effect of time on biological modification.

3.4. Effect of Time. Figure 4 presents the effect of culture time on biological modification. The results showed that the culture time had a considerable influence on the solid fermentation process. In the early stage of culture, the mycelial growth of *Aspergillus niger* was slow with cellulose production, resulting in no modification of the corn stalk. However, with increased culture time, the nutrients in the culture medium were depleted and other metabolites were increased, decreasing the activity of the cellulose and lowering biosorption [19]. It leads to culture time of 72 h, approaching the best modification.

3.5. Effect of Additional Carbon and Nitrogen. Considering the chemical interaction between Cu(II) and glucose (added as C source), 0.08 g glucose was put into 100 mL of $CuSO_4{\cdot}5H_2O$ solution with an initial Cu^{2+} concentration of

20 mg/L. The flasks were shaken at 30°C with 150 rpm for 30 minutes (under the same condition of biosorption). The Cu^{2+} concentration was still 20 mg/L. So, we come to the conclusion that glucose has no influence in the process of biosorption of Cu(II). Figure 5 depicts the effect of different dosages of $(NH_4)_2SO_4$ and glucose on biological modification. The results show that the increasing supplemental nitrogen has a little effect on biological modification but increasing carbon source causes to decrease the biological modification. In addition, the corn stalk is rich in nitrogen and carbon sources. Therefore, it does not need to benefit from additional carbon and nitrogen sources. Thus, our results are clear indication of additional nitrogen and carbon effects.

3.6. Comparison of the Biosorption for Cu^{2+} by Fermented Corn Stalk and Raw Corn Stalk. According to Table 1, under the same conditions, the biosorption of dry raw and fermented corn stalk for Cu^{2+} was compared. The raw corn stalk has 48.3% biosorption rate and 6.44 (mg/g) of biosorption capacity. But fermented corn stalk possesses 93.5% biosorption rate and 12.47 (mg/g) of biosorption. This result manifests that the biosorption capacity of the fermented corn stalk was improved to nearly twice than that of raw corn stalk.

3.7. Regeneration Studies of Fermented Corn Stalk. The effect of regeneration cycles of the fermented corn stalk on the biosorption capacity was constantly tested 3 times, and the results are shown in Table 2. It is seen that the biosorption capacities of fermented corn stalk for Cu(II) were almost not affected, and the regeneration efficiency of the biosorbent was generally high. The results illuminate that the spent fermented corn stalk could be effectively regenerated by HCl and reused at least 3 times without decreasing its biosorption capacity significantly.

3.8. Biosorption of Binary Metal Solutions. In order to test the selectivity of the fermented corn stalk towards the removal of Cu^{2+}, biosorption by introducing other kinds of divalent ions such as Pb^{2+}, Ca^{2+}, and Cd^{2+} was investigated in a single ion solution. When the biosorbent dosage was 0.15 g and the initial concentration was 20 mg/L, the biosorption value of the biosorbents for Cu^{2+} was 12.47 mg/g. However, Figure 6 shows when Pb^{2+}, Ca^{2+}, and Cd^{2+} were added, the biosorption capacities for Cu^{2+} decreased to 9.98, 8.72, and 9.35 mg/g, respectively. The biosorption capacities of the biosorbent in the presence of the binary metal mixture were lower than under noncompetitive conditions.

3.9. FTIR of Fermented Corn Stalk and Raw Corn Stalk. Figure 7 presents FTIR spectra of raw corn stalk and fermented corn stalk before and after biosorption. When comparing corn stalk (a) with fermented corn stalk (b), it is clear that there were some similar biosorption bonds. The IR spectrum exhibits some absorption peaks that are characteristic of cellulose at 3430 cm^{-1}, 2920 cm^{-1}, 1380 cm^{-1}, and 1030 cm^{-1} [20]. The IR spectrum of the fermented corn stalk

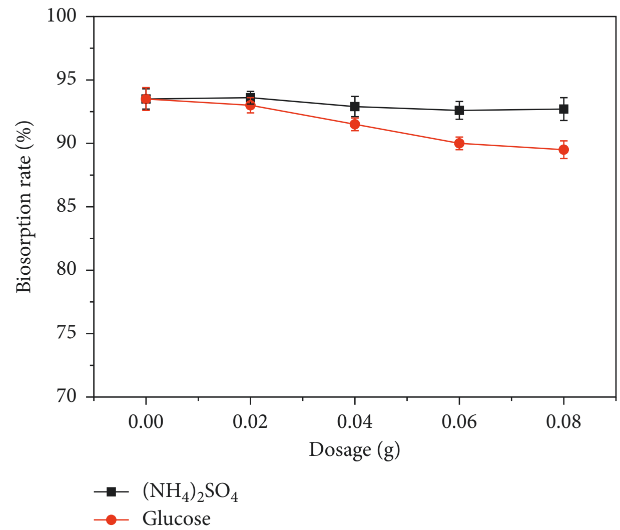

Figure 5: Effect of $(NH_4)_2SO_4$ and glucose dosage on biological modification.

Table 1: Comparison of the biosorption of Cu^{2+} by different dry modified materials.

Biosorption material	Biosorption rate (%)	Biosorption capacity (mg/g)
Raw corn stalk	48.3	6.44
Fermented corn stalk	93.5	12.47

Table 2: The capacity of biosorption and desorption for Cu(II) on fermented corn stalk for three cycles.

Times	Biosorption (mg/g)	Desorption (mg/g)	Recovery rate (%)
1	12.47 ± 0.22	12.32 ± 0.24	98.7
2	12.17 ± 0.24	11.92 ± 0.23	97.9
3	11.87 ± 0.23	11.50 ± 0.22	96.8

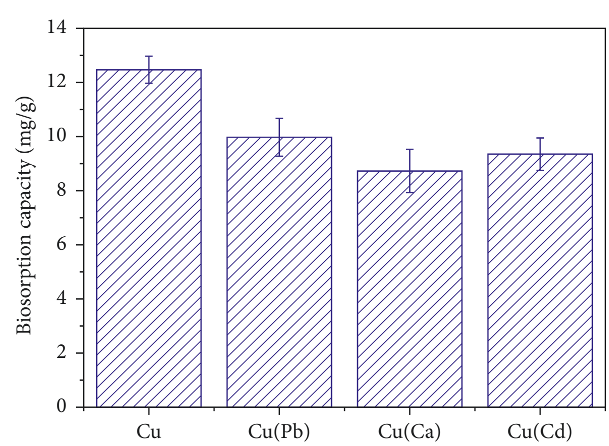

Figure 6: Biosorption capacity for Cu^{2+} and binary metal ion mixtures with other kinds of divalent ions.

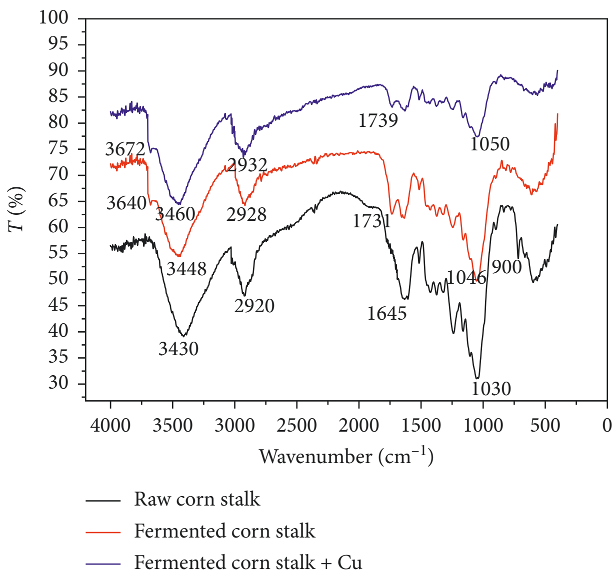

Figure 7: FTIR spectra of modified corn stalk and raw corn stalk.

displayed some differences from that of the raw corn stalk. The fermented corn stalk spectrum has an extra band, peaking at 3640 cm^{-1} which corresponds to free hydroxyl-OH groups. This result may indicate the destruction of the cellulose molecules within the hydrogen bond. Additionally, the peaks at 900 cm^{-1} and 1645 cm^{-1} were not presented for the fermented corn stalk. This may reflect the destruction of the ester structure and the oxidation of the unsaturated C=O bond to become –COOH. The IR results show that the enzymes produced by *Aspergillus niger* degrade some of the celluloses of the corn stalk and oxidize some of the functional groups of the cellulose. Some of the hydroxyl and carboxyl groups bounded by cellulose which become free hydroxyl and carboxyl groups have a high ability to adsorb heavy metals. From curve (c), we see that after biosorption, with the loading of Cu^{2+} ions, there was some shift of peaks in 3640, 3448, 2928, 1731, and 1046 cm^{-1}, so it is presumed that the Cu^{2+} metal ion was incorporated with fermented corn stalk biosorbents through interaction with active functional groups such as –OH, C=O, –C=O, and C=C. Therefore, one can be concluded that the fermented corn stalk has a variety of functional groups such as hydroxyl and carboxyl, as well as groups which are important sites for metal biosorption [21].

3.10. SEM of Fermented Corn Stalk and Raw Corn Stalk. Figures 8(a)–8(c) shows the SEM micrograph of raw corn and fermented corn stalks. After comparing the surface structure of raw corn with fermented corn stalk, the surface structure of fermented corn stalk was destroyed and the surface compactness was also decreased. There are many porosities on the surface of the fermented corn stalk, allowing part of the inner cellulose of the fermented corn stalk to contact enzymes which are produced by *Aspergillus niger*. This causes the release of more functional groups that improve the ability to adsorb heavy metals. Thus, according

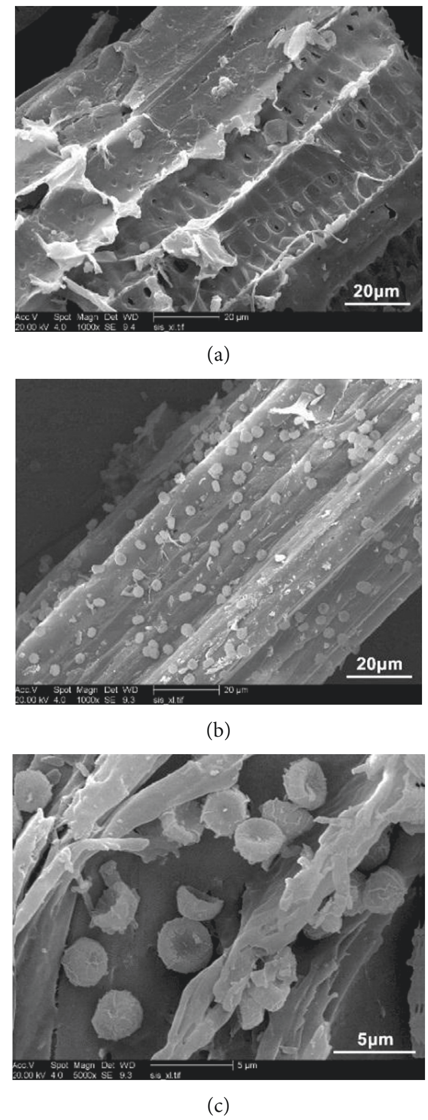

Figure 8: SEM micrographs: (a) raw corn stalk, (b) fermented corn stalk, and (c) closer inspection of Figure 7(b).

to the closer inspection of fermented corn stalk (Figure 7(b)), the Figure 7(c) shows the surface roughness of fermented corn stalk which clearly indicates the porosity on the irregular surface of corn stalk.

4. Conclusion

In this study, fermented corn stalk (FCS) for biosorption of Cu(II) ions from aqueous solution was prepared. The optimal conditions were experimentally investigated as a solid-liquid ratio of 1 : 5, pH of 5.5 with culture temperature of 28°C, and 72 h fermentation time. Under the same biosorption conditions (biosorbent dosage of 0.15 g, natural pH, 100 rpm, 30°C, and 30-minute reaction time), the biosorption capacity of fermented corn stalk (12.47 mg/g) was significantly greater than that of raw corn stalk (6.44 mg/g). SEM and FTIR demonstrated the modification of surface of the fermented corn stalk by *Aspergillus niger* treatment, resulting in different biosorption capacity of the raw corn stalk. The abundant corn stalk adsorption present in renewable resources, such as biological, leads to high selectivity and adsorption capacity. Fermented corn stalk should be the focus on future efforts to develop effective bio-based adsorption materials.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Authors' Contributions

B. Ren and M. K. Shahzad contributed equally and wrote the manuscript. Y. Jin, F. Ouyang, and H. Li directed the work and contributed the data. All authors have given approval to the final version of the manuscript.

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References

[1] A. Y. Dursun, "A comparative study on determination of the equilibrium, kinetic and thermodynamic parameters of biosorption of copper(II) and lead(II) ions onto pretreated *Aspergillus niger*," *Biochemical Engineering Journal*, vol. 28, no. 2, pp. 187–195, 2006.

[2] M. Mukhopadhyay, S. B. Noronha, and G. K. Suraishkumar, "Kinetic modeling for the biosorption of copper by pretreated," *Bioresource Technology*, vol. 98, pp. 1781–1787, 2007.

[3] Y. G. Zu, X. H. Zhao, M. S. Hu et al., "Biosorption effects of copper ions on *Candida utilis* under negative pressure cavitation," *Journal of Environmental Sciences*, vol. 18, no. 6, pp. 1254–1259, 2006.

[4] D. L. Vullo, H. M. Ceretti, M. A. Daniel, S. A. Ramirez, and A. Zalts, "Cadmium, zinc and copper biosorption mediated by *Pseudomonas veronii* 2E," *Bioresource Technology*, vol. 99, pp. 5574–5581, 2008.

[5] W. C. Kao, J. Y. Wu, C. C. Chang, and J. S. Chang, "Cadmium biosorption by polyvinyl alcohol immobilized recombinant *Escherichia coli*," *Journal of Hazardous Materials*, vol. 169, no. 1–3, pp. 651–658, 2009.

[6] K. Tsekova, D. Todorova, V. Dencheva, and S. Ganeva, "Biosorption of copper(II) and cadmium(II) from aqueous solutions by free and immobilized biomass of *Aspergillus niger*," *Bioresource Technology*, vol. 101, no. 6, pp. 1727–1731, 2010.

[7] G. Yan and T. Viraraghavan, "Heavy metal removal in a biosorption column by immobilized *M. rouxii* biomass," *Bioresource Technology*, vol. 78, no. 3, pp. 243–249, 2001.

[8] J. J. Wen, Q. X. Zhang, G. Q. Zhang, and Z. Y. Cao, "Deep removal of copper from cobalt sulfate electrolyte by ion-exchange," *Transactions of Nonferrous Metals Society of China*, vol. 20, no. 8, pp. 1534–1540, 2010.

[9] G. Blazquez, M. A. Martín-Lara, E. Dionisio-Ruiz, G. Tenorio, and M. Calero, "Copper biosorption by pine cone shell and thermal decomposition study of the exhausted biosorbent," *Journal of Industrial and Engineering Chemistry*, vol. 18, no. 5, pp. 1741–1750, 2012.

[10] A. Ronda, M. A. Martín-Lara, E. Dionisio, G. Blazquez, and M. Calero, "Effect of lead in biosorption of copper by almond shell," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 44, no. 3, pp. 466–473, 2013.

[11] S. Yargic, R. Z. Yarbay Şahin, N. Ozbay, and E. Onal, "Sustainable development of energy, water and environment systems," *Journal of Cleaner Production*, vol. 88, pp. 152–159, 2015.

[12] H. Hu, J. Zhang, K. Lu, and Y. Tian, "Characterization of *Acidosasa edulis* shoot shell and its biosorption copper ions from aqueous solution," *Journal of Environmental Chemical Engineering*, vol. 3, no. 1, pp. 357–364, 2015.

[13] S. Vafakhah, M. E. Bahrololoom, and M. Saeedikhani, "Adsorption kinetics of cupric ions on mixture of modified corn stalk and modified tomato waste," *Journal of Water Resource and Protection*, vol. 8, no. 13, pp. 1238–1250, 2016.

[14] Y. T. Wang, H. Chen, D. J. Wang, L. J. Bai, H. Xu, and W. X. Wang, "Preparation of corn stalk- based adsorbents and their specific application in metal ions adsorption," *Chemical Papers*, vol. 70, no. 9, pp. 1171–1184, 2016.

[15] M. N. Sepehr, S. Nasseri, M. Zarrabi, M. R. Samarghandi, and A. Amrane, "Removal of Cr(III) from tanning effluent by *Aspergillus niger* in airlift bioreactor," *Separation and Purification Technology*, vol. 96, pp. 256–262, 2012.

[16] Q. Ren, Y. T. Zhang, L. Y. Zhao, X. C. Zhang, F. J. Ouyang, and H. W. Zhang, "Biosorption of chromium by the spores of *Aspergillus niger*," *International Conference on Mechatronics*, vol. 191, p. 2991, 2015.

[17] M. Dixon, "The effect of pH on the affinities of enzymes for substrates and inhibitors," *Biochemical Journal*, vol. 55, no. 1, pp. 161–170, 1953.

[18] F. Y. Wu, "Study on the condition of fermentation producing cellulase by *Aspergillus niger*," *Chinese Agricultural Science Bulletin*, vol. 25, no. 9, pp. 74–77, 2009.

[19] F. Y. Zhang, Y. Q. Song, and X. W. Cheng, "Study on cellulase production by the fermentation of corn straw stalk using *Aspergillus niger*," *Journal of Shanxi Agricultural University*, vol. 3, pp. 206–210, 2009.

[20] C. F. Liu, F. Xu, J. X. Sun et al., "Physicochemical characterization of cellulose from perennial ryegrass leaves (*Lolium perenne*)," *Carbohydrate Research*, vol. 341, no. 16, pp. 2677–2687, 2006.

[21] W. O'Connell, C. Birkinshaw, and T. F. O'Dwyer, "Heavy metal adsorbents prepared from the modification of cellulose," *Bioresource Technology*, vol. 99, no. 15, pp. 6709–6724, 2008.