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Selectively Desirable Rapeseed and Corn Stalks Distinctive for Low-Cost Bioethanol Production and High-Active Biosorbents

Chengbao Xu[1,2] · Tao Xia[1,3] · Jintong Wang[1,3] · Li Yu[4] · Leiming Wu[1,2] · Yanqing Zhang[1,3] · Peng Liu[1,2] · Peng Chen[1,2] · Shengqiu Feng[1,2] · Liangcai Peng[1,2]

Abstract

Crop straws provide large amounts of biomass resource for biofuels, but it remains to explore cost-effective lignocellulose process technology with additional valuable bioproducts. Using total eight rapeseed and corn stalks with distinct lignocellulose composition, this study initially performed mild alkali pretreatment (1% NaOH, 50 °C) for enzymatic hydrolysis and yeast fermentation to release bioethanol yields varied from 5 to 12% (% dry matter). By comparison, four corn stalks consistently showed more ethanol yields than those of the rapeseeds, but relatively higher sugar-ethanol conversion rates were examined in the rapeseed samples. Of all stalk samples, both genetic corn mutant (CY04) and classic rapeseed cultivar (Bn18) were respectively assessed as the desired lignocellulose residues for relatively high bioethanol production. Then, all remained solid residues of yeast fermentation were employed as biosorbents for Cd adsorption under various incubation conditions (pH, temperature, time, Cd concentration, biosorbent dose). In general, the solid residues exhibited much higher Cd adsorption capacities and removal rates than those of the raw stalks. In particular, two desirable rapeseed residues were of the highest Cd adsorption capacities, compared to the corn residues examined in this study or other major agricultural crop straws as previously reported. Furthermore, the solid residues were characterized as typical biosorbents via a classic chemical binding manner with much large surface areas accountable for their high Cd adsorption capacity. Therefore, this study has demonstrated a green-like strategy for low-cost cellulosic ethanol production and high-active biosorbents by selecting desired corn and rapeseed stalks.

Graphic Abstract
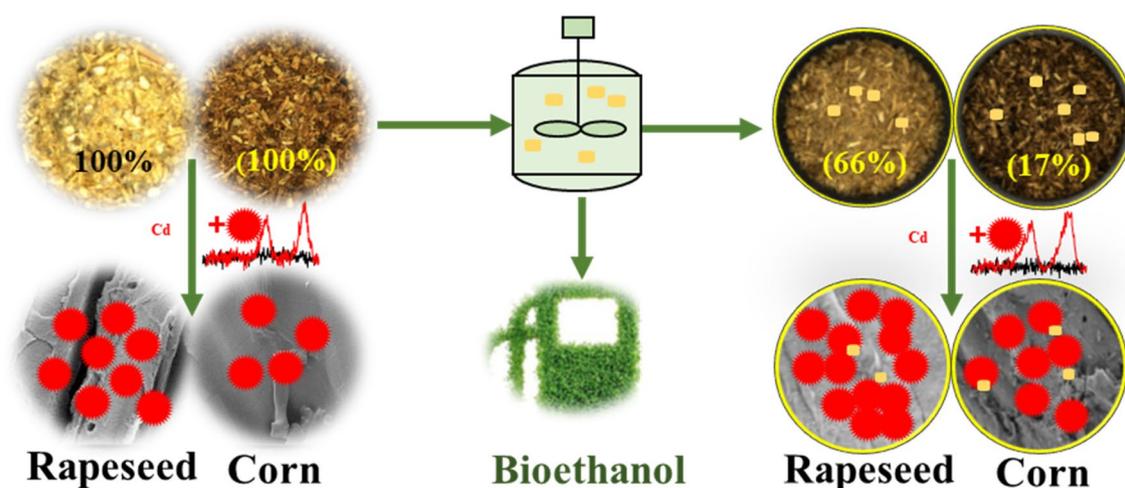
Extended author information available on the last page of the article

Statement of Novelty

It has been well considered that high-cost and secondary pollution are two crucial issues that determine current lignocellulose process unacceptable for large-scale bioethanol production. Hence, this study performed a mild alkali pretreatment with eight distinct rapeseed and corn stalks, and obtained the highest bioethanol yield in the desirable genetic corn mutant. Then, the remained solid residues of yeast fermentation were applied as biosorbents for heavy metal removal, and the biosorbents of best-performance were sorted out in two desirable rapeseed stalks. To our knowledge, this study has at the first time demonstrated a greenlike strategy simultaneous for low-cost cellulosic ethanol production and high-active biosorbents using desired corn and rapeseed stalks, leading to efficient bioethanol process and value-added biosorbent application.

Introduction

Bioethanol has been well evaluated as a perfect additive into gasoline with less net carbon release into the environment, and lignocellulose residues of agricultural crops are thus considered as enormous biomass resource convertible for bioethanol and bio-chemicals [1, 2]. As the promising second generation of biofuel, the lignocellulose-derived bioethanol production mainly involves in three steps: initial physical and chemical pretreatments for wall polymer destruction, sequential enzymatic hydrolysis for soluble sugar release, and final yeast fermentation for bioethanol product [3]. However, due to lignocellulose recalcitrance, biomass process requires strong pretreatment conditions, leading to an unacceptably costly bioethanol conversion with potential secondary waster release [4, 5]. Hence, it remains important not only to find out a cost-effective bioethanol conversion technology, but also to use or recycle all remained biomass residues for any value-added bioproducts [6, 7].

Heavy metals are toxic to human beings and animals due to their non-biodegradable at trace concentration [8]. Among the heavy metals, cadmium (Cd) has been regarded as one of the most hazardous substances [9] and it could pollute agricultural land, water source and other daily-life location [10]. Over the past years, many conventional technologies have been established to remove Cd from various polluted sources [11, 12], but the most techniques are highly costly with potential secondary waste release [13]. It is thus interesting to explore if the biomass wastes could be applicable for efficient adsorption of Cd and other heavy metals.

The adsorption process for removal of heavy metals has been conducted using the high specific surface area of activated sludge or the chemically-modified biomass residues or industry by-products [14]. In particular, the nonviable biomass could be applied as biosorption by binding and concentrating heavy metals from aqueous solutions [15]. Although biosorption is an efficient technology for removal of heavy metals [16], it becomes critical to search for the biosorbents that are of low-cost, high-activity and well-performance [17]. Therefore, as biomass residues could be modified as active biosorbents, it would be important to evaluate the ideal biomass wastes obtained from bioethanol process of major crop stalks.

Rapeseed is a typical oil plant and corn is a major grain crop over the world, but both crops could annually produce billions tons of lignocellulose residues [18]. In this study, we initially performed mild alkali pretreatments with total eight distinct rapeseed and corn stalk samples, and compared their biomass saccharification and bioethanol yields. In terms of bioethanol production achieved from all crop stalks, we selected out four representative biomass samples, and evaluated the remained solid residues of yeast fermentation by testing their adsorption capacity with Cd under various conditions (pH, initial concentration, temperature, etc). Furthermore, we performed a characteristic assay of the remained solid residues using X-ray photoelectron spectroscopy (XPS), in order for understanding of why the remained solid residues were of high-activity and well-performance during the Cd adsorption process. Hence, this study primary achieved low-cost cellulosic ethanol production under mild alkali pretreatments with eight distinct rapeseed and corn stalks, and subsequently sorted out the high-active biosorbents by evaluating the remained solid residues of yeast fermentation in the desirable crop stalks.

Materials and Methods

Sample Collection

Two cultivars (CZ31, CM01) and two genetic mutant (CY18, CY04 [19]) of corn were grown in the experimental field of Huazhong Agricultural University, Wuhan, China in 2016 and their mature stalks were collected. Four rapeseed cultivars (Bc01, Bj05, Bn18, Bn06) were grown in Hubei experimental field in 2013 [20]. The mature stalks of total eight corn and rapeseed samples were collected, crushed using a knife-mill and stored in the dry container until use.

Alkali Pretreatment and Biomass Enzymatic Hydrolysis

All used chemicals were analytical grade, except the chemicals of adsorption experiments at guarantee reagent, which was used without further purification unless otherwise mentioned. The alkali pretreatment (1.0% NaOH, at 50 °C, 150 rpm for 2 h) was performed in all eight biomass samples as previously described by Zahoor et al. [21] and Pei et al. [20]. For sequential enzymatic hydrolysis, all pretreated biomass residues were incubated with the final concentration of 1.6 g/L mixed-cellulases (10.6 FPU/g biomass) and xylanase (6.72 U/g biomass) purchased from Imperial Jade Bio-technology Co., Ltd co-supplied with 1% Tween-80 as previously described by Jin et al. [22]. All experiments were conducted in biological triplicate.

Yeast Fermentation and Ethanol Measurement

Yeast fermentation was conducted using total hexoses released from alkali pretreatment and sequential enzymatic hydrolysis and *Saccharomyces cerevisiae* strain (Angel yeast Co., Ltd., Yichang, China), and the released ethanol was measured as previously described by Li et al. [23]. All experimental assays were performed with biological triplicate.

Adsorption Analysis Using All Solid Residues of Ethanol Fermentation

All remained solid residues from ethanol fermentation were washed with distilled water three times, followed with ultra-pure water for another three times. The remained residues were collected, dried at 50 °C in an air oven and stored as biosorbents for the following experiments. Solutions of Cd^{2+} was prepared by adding $Cd(NO_3)_2$ into ultra-pure water, and stored at room temperature. Batch adsorption experiments with biosorbents were performed for 4.0 h in 50 mL tubes at 150 rpm. After stirring, the samples were filtered through a 0.45 μm membrane filter and the residual Cd^{2+} concentration in the filtrate was determined by flame atomic adsorption spectrophotometer (FAAS HITACHI Z-2000, Japan) equipped with air–acetylene flame. The amount of adsorption at equilibrium q_e (mg g^{-1}) and the percentage removal efficiency (%R) were calculated according to Eqs. 1 and 2:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where C_0 and C_e are the initial and equilibrium solution concentrations of Cd^{2+} (mg L^{-1}), respectively. V (L) is the volume of the solution, and W (g) is the weight of the used biosorbent, and q_e is the equilibrium adsorption capacity (mg g^{-1}). During the adsorption process, dependence of the initial concentration, adsorbent dose, contact time, temperature, and pH on the adsorption behavior was measured thoroughly. The corresponding supernatants were immediately centrifuged, collected, and diluted for concentration analysis by FAAS. Biosorption experiments for each metal were performed under the same operating condition: pH (4.0–8.0), contact time (1–240 min), adsorbent dose (0.2–1.8 g L^{-1}), initial metal concentration (2.0–40.0 mg L^{-1}) and temperature (15–45℃). All experiments were conducted in biological triplicate.

Langmuir isotherm model is expressed as Eq. 3:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \tag{3}$$

where C_e is the equilibrium concentration of the adsorbate (mg L^{-1}), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg g^{-1}), q_{max} is the theoretical maximum monolayer adsorption capacity of the adsorbent (mg g^{-1}), and b is the Langmuir isotherm constant related to the adsorption energy (L mg^{-1}).

As another typical simulation model for adsorption, the Freundlich isotherm is often used for non-ideal adsorption that involves heterogeneous surface energy system. It is described as Eq. 4:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}$$

where K_F (L mg^{-1}) is the Freundlich adsorption constant, and 1/n is a measure of the adsorption intensity that determines whether the adsorption intensity and type of isotherm is favorable (0.1 < 1/n < 0.5) or unfavorable (1/n > 2).

The linear form of the pseudo-second-order equation is computed as Eq. 5:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

Here k_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}). The values of t/q_t are plotted against t, and the predicted adsorption capacity q_e (mg g^{-1}) and k_2 are calculated from the slope and intercept of the plot, respectively [24].

Characterization of Biosorbents

The Cd^{2+} inter-linkage style with solid residues and raw materials were characterized by X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo fisher, USA) as

previously described by Moulder et al. [25]. Surface area measurements were conducted on a Quantachrome Instruments' Autosorb-iQ surface area analysis and porosimetry analyzer as previously described by Wang et al. [26].

Wall Polymer Assay

Plant cell wall fractionation procedure was performed to extract hemicelluloses and cellulose fractions as previously described by Peng et al. [27]. UV–VIS Spectrometer (V-1100D, Shanghai MAPADA Instruments Co.) was used for hexoses and pentoses assay as previously described by Huang et al. [28]. For cellulose assay, sample was dissolved in 67% H_2SO_4 and hexoses was detected by the anthrone/H_2SO_4 method to calculate cellulose level. Hemicelluloses were calculated by determining total hexoses and pentoses of the hemicellulose fraction. In addition, total lignin assay was measured by two-step acid hydrolysis method according to the Laboratory Analytical Procedure of the National Renewable Energy Laboratory [20]. All experimental analyses were performed in biological triplicates.

Results and Discussion

Varied Biomass Saccharification and Bioethanol Production in Rapeseed and Corn Stalks

This study initially performed mild alkali pretreatments (1% NaOH at 50 °C for 2 h) with the mature stalks of total eight rapeseed and corn cultivars that showed distinct cell wall compositions including cellulose, hemicelluloses and lignin (Table 1). Using our previously-established approach [29], we detected biomass saccharification by measuring hexoses yield (% cellulose) released from enzymatic hydrolysis of the pretreated biomass residues [30] (Fig. 1a, b). In general, total eight rapeseed and corn stalks exhibited largely varied hexoses yields from 16 to 78% (% cellulose) released from enzymatic hydrolysis (Fig. 1a, b). In comparison, all four

Table 1 Cell wall compositions (% dry matter) of rapeseed and corn straws

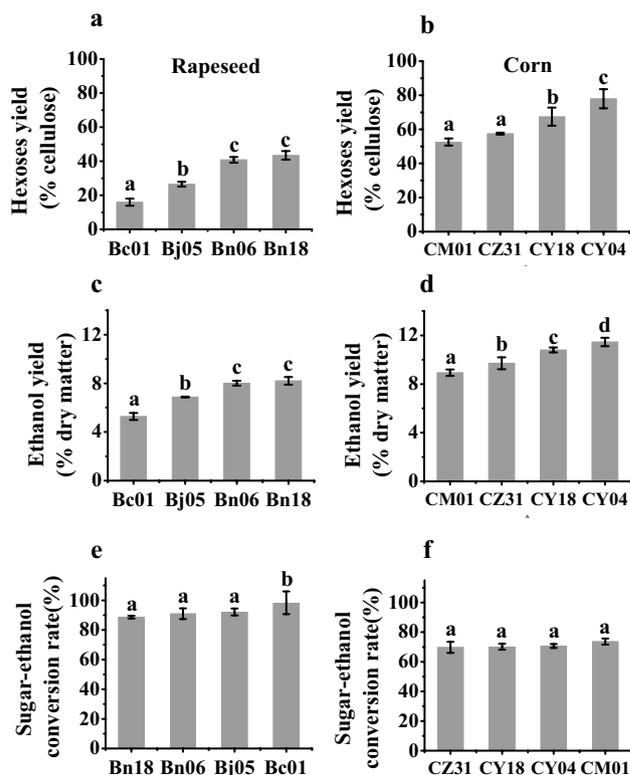| No.	Cellulose	Hemicellulose	Lignin
Bc01	33.17 ± 0.29	23.98 ± 0.50	22.49 ± 0.73
Bj05	36.69 ± 0.74	24.02 ± 0.76	23.10 ± 0.66
Bn18	32.48 ± 0.12	23.41 ± 0.39	15.63 ± 0.26
Bn06	32.27 ± 0.77	22.95 ± 0.26	15.87 ± 0.58
CM01	38.76 ± 0.20	24.49 ± 0.96	21.05 ± 0.35
CZ31	38.36 ± 0.81	19.70 ± 0.70	20.59 ± 0.65
CY18	23.35 ± 0.73	21.30 ± 0.80	28.01 ± 0.79
CY04	20.41 ± 0.73	14.74 ± 0.44	30.17 ± 0.17

Fig. 1 Biomass saccharification and bioethanol production in rapeseed and corn stalks under mild alkali pretreatment. **a**, **b** Hexoses yields (% cellulose) released from enzymatic hydrolysis after 1.0% NaOH pretreatment with rapeseed and corn stalks. **c**, **d** Bioethanol yields (% dry matter) obtained by yeast fermentation using total hexoses released from enzymatic hydrolyses and biomass pretreatment. **e**, **f** Sugar–ethanol conversion rates. Data as means ± SD (n = 3). Letters (a, b, c) of the bars as significantly different groups (p < 0.05)

corn samples had much higher hexoses yields (53–78%) than those of the rapeseed samples (16–43%), which should be mainly due to relatively less lignin and cellulose contents in corn samples [23]. The results were also consistent with the previous reports of relatively low biomass saccharification in rapeseed stalks.

As a consequence, this study conducted a classic yeast fermentation using all hexoses released from both alkali pretreatment and enzymatic hydrolysis (Fig. 1c, d). Due to their varied hexoses yields, total eight rapeseed and corn samples produced the ethanol yields ranged from 5 to 12% (% dry matter), and all four corn samples remained significantly higher ethanol yields than those of the rapeseed. In particular, the classic rapeseed cultivar (Bn18) and corn genetic mutant (CY04) samples were of the highest bioethanol yields among all rapeseed and corn stalks. In addition, four corn samples had similar sugar-ethanol conversion rates, whereas only one rapeseed sample (Bc01) showed significantly higher conversion rate than other three rapeseeds did (Fig. 1e, f). However, all rapeseed samples showed much

higher sugar-ethanol rates than those of the corn samples, suggesting that the mild alkali pretreatment should release relatively less inhibition compounds of yeast fermentation in the rapeseed samples [31]. On the other hands, despite the mild alkali pretreatment led to relatively less biomass saccharification and lower bioethanol yield, it was of two advantages: cost-effective bioethanol process and more biomass residues for high-active biosorbents as described below.

Increased Cd Adsorption with the Solid Residues of Yeast Fermentation Under Different pH Conditions

Although biomass residues have been processed as biosorbents for heavy metals adsorption [32, 33], little is known about utilization of the remained solid residues of yeast fermentation including undigested lignocellulose and yeast cells. In this study, we examined that four rapeseed samples remained about 49–66% (of total dry weight) solid biomass residues after yeast fermentation and the four corn samples only had 12–17% residues (Fig. 2a, b), consistent with their distinct biomass saccharification and ethanol production (Fig. 1). Hence, despite that the rapeseed samples produced relatively lower bioethanol yields than those of the corn under mild alkali pretreatment, they remained much more solid biomass residues applicable as biosorbents. Based on the information of hexoses and bioethanol yields among all eight samples (Fig. 1), we selected two pairs of representative rapeseed (Bc01, Bn18) and corn (CZ31, CY04) samples that showed relatively low and high hexoses and ethanol yields, which will be employed for the following Cd adsorption experiments. Because the pH value of the initial

solution is one of the most important parameters affecting the adsorption process [34], this study performed an adsorption analysis with Cd^{2+} by comparing solid biomass residues of yeast fermentation with their raw stalk materials under different pH values (Fig. 2c–f). To avoid $Cd(OH)_2$ precipitation during the Cd^{2+} adsorption, experiments were carried out at pH 4.0–8.0 values [35]. In comparison, all four solid biomass residues of yeast fermentation had much higher Cd^{2+} adsorption rates than those of their raw stalk materials, except the raw material of Bn18 showing slightly lower adsorption capacity than its solid residue (Fig. 2e). In particular, four solid residues of rapeseed and corn almost reached to the maximum adsorption rate of 100% at pH 8, whereas all solid residues and raw materials had the lowest adsorption rates at pH 4, which should be mainly due to the acidic condition that led to relatively high H^+ concentration competitive with the Cd^{2+} for the adsorption site on the surface of the biosorbents. On the other hands, as pH values remained increasing, all samples exhibited remarkably raised adsorption rates, due to the decrease of H^+ concentration beneficial to the combination of Cd^{2+} with biosorbents [36]. Hence, the different pH values may affect the dissociation state of related groups among cellulose, hemicellulose, lignin and pectin particularly in the solid residues of yeast fermentation, which should be partially accountable for their adsorption rates [37].

High Adsorption Capacity with Solid Residues Under a Series of Cd Concentration

To further examine the Cd adsorption capacity, this study used four concentrations of Cd to incubate with the solid residues and raw materials of rapeseed and corn samples

Fig. 2 Comparison of Cd adsorption rates under different pH values between the solid residues and raw materials in representative rapeseed and corn samples. **a**, **b** Percentages of solid residues (of total raw materials) after yeast fermentation. **c**, **d** Cd adsorption rates in two rapeseed (Bc01, Bn18) samples. **e**, **f** Cd adsorption rates in two corn (CZ31, CY04) samples. Incubation conditions: $C_0 = 2$ mg L^{-1}, adsorbent dose = 1 g L^{-1}, T = 25 ± 2 °C, t = 4.0 h
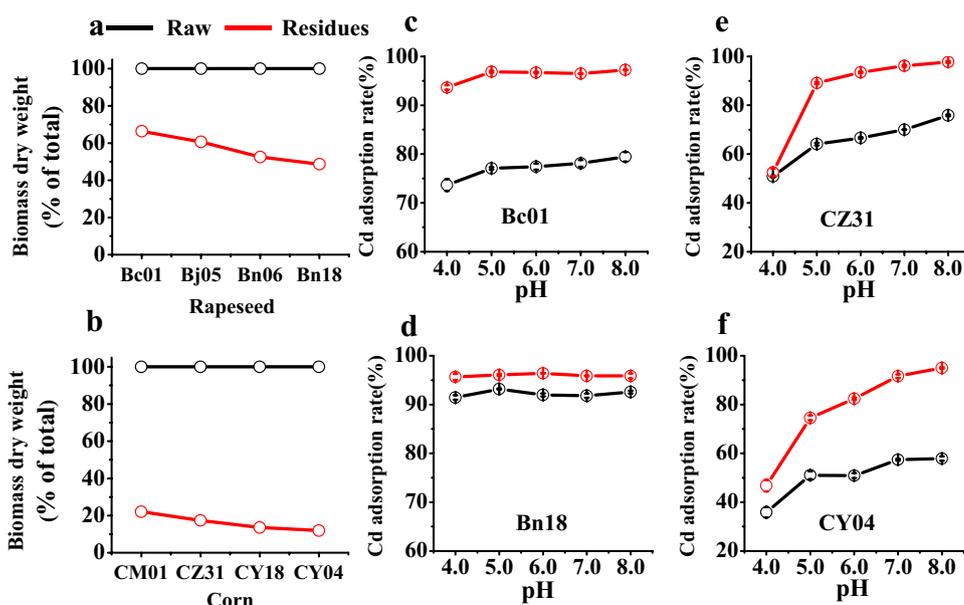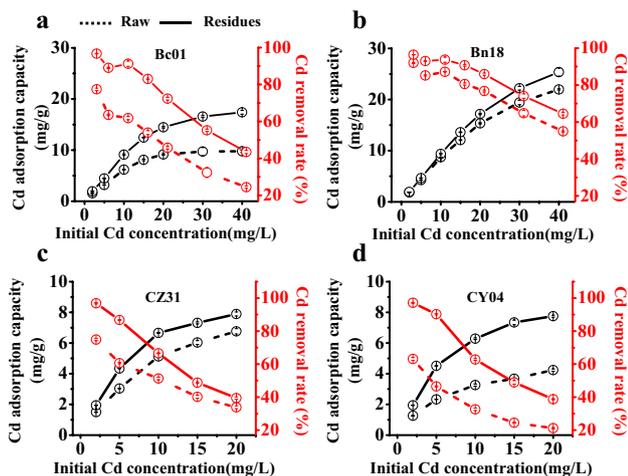
Fig. 3 Cd adsorption capacity and removal rates under initial Cd concentrations between the solid residues and raw materials in representative rapeseed (Bc01, Bn18) and corn (CZ31, CY04) samples. Incubation conditions: **a**, **b** pH 6.0, adsorbent dose = 1 g L^{-1}, T = 25 ± 2 °C, t = 4.0 h); **c**, **d** pH 8.0, adsorbent dose = 1 g L^{-1}, T = 25 ± 2 °C, t = 4.0 h

(Fig. 3). As a result, all samples showed a consistently increasing Cd^{2+} adsorption capacity as the incubated Cd concentration was raising, leading to a constantly reducing Cd^{2+} removal rate. This should be due to the high concentration of metal ion that could provide more driving force for adsorption and thereby overcoming the mass transfer resistance of the metal [38]. Consistent with the Cd adsorption assay under different pH values, the solid residues of rapeseed and corn also showed significantly higher Cd adsorption capacity or removal rates than those of their raw materials under different Cd concentrations incubated in this study. Accordingly, two rapeseed samples (Fig. 3a, b) remained higher Cd^{2+} adsorption capacity than those of

two corn samples (Fig. 3c, d) in both solid residues and raw materials. In addition, the Bn18 sample was of the highest Cd adsorption capacity and removal rate in both solid residue and raw material among all four rapeseed and corn samples examined.

Furthermore, this study measured the Cd^{2+} adsorption isotherm, and all samples showed a regular shape with a steep initial slope, indicating that both solid residues and raw materials could act as a high efficacy biosorbent at low Cd^{2+} concentration. Therefore, those batch experimental data were further applied into the Langmuir and Freundlich isotherm equations as previously described by Aksu et al. [39], and the fitting parameters were presented in Table 2. On the basis of the correlation coefficients, the Langmuir model showed the R^2 value > 0.98, suggesting that the adsorption of Cd^{2+} could be even better described by the Langmuir model. The results thus revealed that all adsorption sites were homogeneously distributed over the external and porous surfaces of materials in all solid residues and raw materials of rapeseed and corn samples [40].

In addition, compared with other biomass residues as previously reported, the solid resides of two rapeseed cultivars were of much higher Cd adsorption (Table 3) [41–47]. However, because it has been characterized that chemical and physical modification could largely increase adsorption capacity of biomass residues [40, 48], it remains interesting to modify solid residues of the desirable rapeseed stalks in the future studies, which may lead to a maximum adsorption capacity for Cd and other heavy metals.

Distinct Cd Adsorption Capacity Under Different Substrate Doses and Incubation Temperatures

Because all solid residues of rapeseed and corn samples were applicable as active biosorbents described above, this

Table 2 Cd adsorpation Langmuir and Freundlich isotherm model

Sample	Langmuir			Freundlich		
	q_{max} (mg/g)	b (L/mg)	R^2	K_F	1/n	R^2
Bc01						
Raw	10.93	0.34	0.9947	2.64	0.46	0.9194
Residues	18.15	0.87	0.9982	6.67	0.39	0.9105
Bn18						
Raw	25.19	0.35	0.9934	5.78	0.54	0.9538
Residues	27.40	0.71	0.9963	8.87	0.49	0.9387
CZ31						
Raw	7.45	0.43	0.9959	2.17	0.46	0.9737
Residues	8.06	1.98	0.9973	4.15	0.19	0.9245
CY04						
Raw	4.76	0.38	0.9897	1.49	0.39	0.9890
Residues	7.91	2.14	0.9962	4.47	0.25	0.9571

Table 3 Comparison of Cd sorption capacities of various biosorbents (mg/g)

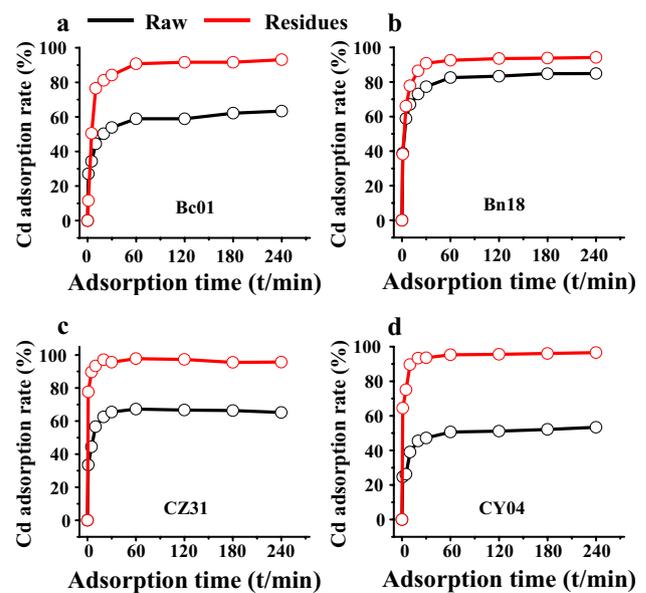| Materials	q_e (mg/g)	References
Bc01 Residues	18.15	This work
Bn18 Residues	27.40	
CZ31 Residues	8.06	
CY04 Residues	7.91	
Modified orange peel	2.91	[41]
Araucaria heterophylla	9.25	[42]
Modified corn straw	12.73	[43]
Wheat straw	14.56	[44]
Rice straw	13.9	[45]
Rice husk ash	3.04	[46]
Wheat straw	3.8	[47]

Fig. 4 Cd adsorption rates during incubation time course between the solid residues and raw materials in representative rapeseed (Bc01, Bn18) and corn (CZ31, CY04) samples. Incubation conditions: **a**, **b** ($C_0 = 10$ mg L^{-1}, original pH 6.0, adsorbent dose = 1 g L^{-1}, $T = 25 \pm 2$ °C, t = 4.0 h); **c**, **d** $C_0 = 2$ mg L^{-1}, original pH 8.0, adsorbent dose = 1 g L^{-1}, $T = 25 \pm 2$ °C, t = 4.0 h

study examined the adsorption capacity under different doses of biosorbents (E-supplementary data of this work can be found in online version of the paper). In general, all biosorbents (solid residues and raw materials) remained a reducing Cd^{2+} adsorption capacity as their doses were increasing, leading to a relatedly raising Cd^{2+} removal rate [49]. Furthermore, although three solid residues (Bc01, CZ31, CY04) were of significantly higher Cd^{2+} adsorption capacities than those of their raw materials under various doses incubated in this study, all four solid residues showed much higher Cd^{2+} removal rates relative to their raw materials. Meanwhile, total four solid residue and raw material samples of rapeseeds exhibited remarkably increased Cd^{2+} adsorption capacities up to 4–8 folds, compared to the four corn samples under different doses, which further indicated that the biosorbents of rapeseed samples persisted much higher Cd^{2+} adsorption capacities than those of the corn samples under various conditions examined in this study. Notably, the Bn18 was of the highest adsorption capacity and removal rate among all samples examined. Hence, the Bn18 should be the desirable cultivar not only for relatively higher bioethanol yield than those of other rapeseed cultivars, but it also should be the optimal biosorbent for the highest Cd adsorption among the rapeseed and corn samples. Relatively, the CY04 samples had the highest bioethanol yields among all rapeseed and corn samples, and it only showed higher Cd adsorption capacity than those of other corn cultivars, rather than the rapeseed samples. Hence, the Bn18 of rapeseed and CY04 of corn should be selected as the desirable stalks for efficient Cd adsorption and relatively high cellulosic ethanol coproduction.

Meanwhile, this study examined the incubation temperature impact on the Cd^{2+} adsorption rates of biosorbents (E-supplementary data of this work can be found in online version of the paper). Among the ranges of 15–45 °C, we observed slightly altered Cd^{2+} adsorption rates in all

biosorbent samples, but the solid residues consistently showed significantly higher Cd^{2+} adsorption rates than those of their raw materials. Therefore, compared to other Cd^{2+} adsorption conditions examined above, the incubation temperature should not be a major factor.

Consistently High Adsorption Rates During the Cd Incubation Equilibriums

It has been characterized that the adsorption and desorption rates could attain an equilibrium state during a long incubation time course [38, 50]. In this study, both solid residues and raw materials were employed to contact with the Cd-bearing solution for different time periods (1, 5, 10, 20, 30, 60, 120, 180, 240 min). We measured the amounts of Cd^{2+} adsorbed (q_t) versus the contact time with various initial Cd concentrations (Fig. 4). Initially, the adsorption processes remained fast, because more than 50% of total Cd^{2+} in solution were removed within the 5 min of contact. At the 60 min, all samples reached to the saturated adsorption state. Afterwards, the slow Cd^{2+} adsorption should involve in the rearrangement of the adsorbed Cd^{2+} on the surface for a more thorough utilization of the adsorption sites in biosorbents [40], suggesting that one hour contacting time should be optimal for Cd^{2+} adsorption. Notably, the fours solid residues exhibited much higher Cd adsorption rates than their raw materials, and the raw material of rapeseed

(Bn18) remained high adsorption relative to other three raw materials, which were consistent with the findings described above.

Kinetic models are commonly used to understand biosorption mechanism, and the quasi-secondary model has been well characterized to account for the adsorption process [51]. In this work, the pseudo-second-order kinetics were characterized using the data obtained (Fig. 4), and all related parameters were calculated (Table 4). Significantly, all eight rapeseed and corn samples showed much high correlation coefficients with R^2 values of more than 0.99, and the calculated q_e values agreed well with experimental q values, suggesting that the experimental data should fit with the pseudo-second-order analysis [52]. Thus, it revealed that the biosorbents of rapeseed and corn should be mainly involved in chemical adsorption process [45].

Slight Impact of Yeast Cells on Cd Adsorption

As the solid residues contained yeast cells and undigested lignocellulose after ethanol fermentation, this study determined yeast content in the solid residues of four rapeseed and corn samples (Fig. 5a). By comparison, two rapeseed solid residues contained 3% yeast cells (% total), whereas two corn samples respectively covered yeast cells at 18%

and 28%. Then, this study performed the adsorption experiments using yeast cells, undigested lignocellulose and solid residues (total undigested lignocellulose and yeast cells). Under the optimal adsorption conditions of rapeseed solid residues ($C_0 = 10.0$ mg L^{-1}, pH 6.0, adsorbent dose = 1.0 g L^{-1}, T = 25 ± 2 °C, t = 4 h) as described above, the Cd^{2+} adsorption capacities of yeast cells, undigested lignocellulose and solid residues in Bc01 sample were respectively determined at 7.9, 9.41, and 9.12 mg/g (Fig. 5b). Despite yeast cells showed relatively lower adsorption capacity, it did not significantly affect the adsorption capacity of solid residues, due to yeast cells only covering 3% of total dry weight. Meanwhile, based on the optimal adsorption conditions of corn residues ($C_0 = 2.0$ mg L^{-1}, pH 8.0, adsorbent dose = 1.0 g L^{-1}, T = 25 ± 2 °C, t = 4 h), the yeast cells, undigested lignocellulose and solid residue of CZ31 sample were determined with the adsorption capacities at 1.85, 1.89, and 1.94 mg/g, respectively (Fig. 5c). Hence, regardless of 31% yeast cells of total dry weight, it did not alter Cd adsorption capacity of solid residue, due to a similar adsorption capacity between yeast cells and undigested lignocellulose residues in the CZ31 corn sample. Taken together, this study examined that yeast cells were active for Cd adsorption, and the solid residues of yeast fermentation could act as high active biosorbents for Cd adsorption in both rapeseed and corn samples [53].

Characteristics of Biosorbents in Rapeseed and Corn Stalks

XPS has been well applied to detect metal element interlinkage style with biosorbents [54]. In this study, we observed two typical peaks in both solid residues and raw materials of rapeseed and corn incubated with Cd^{2+} adsorption solution, whereas the blanks (without Cd^{2+}) did not show those peaks (Fig. 6). Because the absorption peaks appeared in the spectrum of 410.8 eV and 404.9 eV have been respectively characterized as 3d(Cd) and Cd–O linkage (BE Lookup Table for Signals from Elements and Common Chemical Species), the data revealed that the Cd^{2+} should be tightly linked to the biosorbants (solid residues, raw materials) by chemical bonds. Meanwhile, we observed that the peaks of C and O

Table 4 Kinetic parameters of the pseudo-second-order equation

	q (mg/g)	k_2 (g/min·mg)	q_e (mg/g)	R^2
Bc01				
Raw	6.34	0.040	6.36	0.9990
Residues	9.31	0.032	9.41	0.9995
Bn18				
Raw	8.49	0.054	8.55	0.9998
Residues	9.42	0.071	9.47	0.9999
CZ31				
Raw	1.35	1.01	1.32	0.9997
Residues	1.86	1.81	1.83	0.9996
CY04				
Raw	1.07	0.293	1.07	0.9995
Residues	1.93	0.650	1.93	1.0000

Fig. 5 Cd adsorption capacity of yeast cells, undigested lignocellulose and solid residues (yeast cells and undigested lignocellulose). **a** Percentage of yeast cell dry weight after fermentation (% of total solid residue). **b** Cd adsorption capacity of yeast cells and rapeseed samples. **c** Yeast cells and corn samples
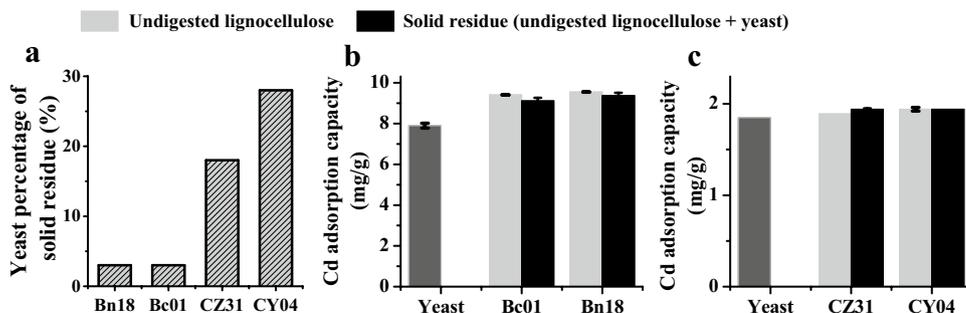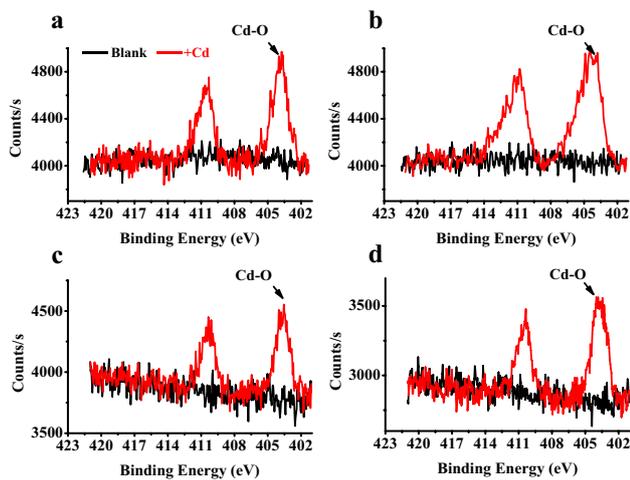
Fig. 6 XPS of Cd 3d spectrum on the solid residues and raw materials incubated with Cd in rapeseed and corn samples. **a**, **b** Raw material and solid residues of rapeseed (Bc01) samples. **c**, **d** Raw material and solid residues of corn (CZ31) samples

Table 5 Detection of surface areas in solid residues and raw materials

Material	Surface area (m^2/g)	
	Raw	Residue
Bc01	43.213	59.605
CZ31	1.047	34.239

Conclusion

In this study, mild alkali pretreatments were performed with eight distinct rapeseed and corn stalks for cost-effective bioethanol production, and in particular, the desirable corn mutant (CY04) achieved the highest bioethanol yield of 12% (% dry biomass). Notably, compared to all raw stalks, the solid biomass residues remained from yeast fermentation were examined as the biosorbents of lower-cost, higher-active and better-performance for Cd adsorption via a classic chemical binding. Therefore, this study has demonstrated an applicable strategy to achieve both low-cost cellulosic ethanol production and value-added biosorbents by using the desirable corn and rapeseed stalks without any waste release into the environment.

elements were distinctively shifted in the solid residues and raw materials incubated with the Cd^{2+} adsorption solution relative to the blanks, suggesting that C 1s and O 1s binding energy should be changed due to the Cd^{2+} adsorption [55], reconfirming a chemical binding between Cd^{2+} and biosorbants.

To further understand why biosorbents of solid residues had higher Cd adsorption capacity than those of raw materials, this study determined their surface areas (Table 5). In comparison, the solid residues exhibited much higher surface areas than those of their raw materials in both rapeseed and corn samples, confirming that the solid residues should be of more functional groups for Cd adsorption [56]. Meanwhile, this study also determined that the rapeseed samples had larger surface areas than those of the corn samples in both solid residues and raw materials, which should be other reason why the rapeseed biosorbents were of higher Cd adsorption capacity relative to the corn ones. In addition, this study detected wall polymer proportions remained in the solid residues. Due to their much less enzymatic saccharification (Fig. 1), the solid residues of rapeseed samples contained much more wall polymers than those of corn samples in particular on lignin and cellulose, which may be additional factor to account for higher Cd adsorption capacity in the solid residues of rapeseed samples.

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Affiliations

Chengbao Xu[1,2] · Tao Xia[1,3] · Jintong Wang[1,3] · Li Yu[4] · Leiming Wu[1,2] · Yanqing Zhang[1,3] · Peng Liu[1,2] · Peng Chen[1,2] · Shengqiu Feng[1,2] · Liangcai Peng[1,2]

✉ Liangcai Peng
lpeng@mail.hzau.edu.cn
http://bbrc.hzau.edu.cn

[1] Biomass and Bioenergy Research Centre, Huazhong Agricultural University, Wuhan, China

[2] College of Plant Science and Technology, Huazhong Agricultural University, Wuhan, China

[3] College of Life Science and Technology, Huazhong Agricultural University, Wuhan, China

[4] Key Laboratory of Biology and Genetic Improvement of Oil Crops and Key Laboratory of Detection for Mycotoxins, Ministry of Agriculture, Oil Crops Research Institute, Chinese Academy of Agricultural Sciences, Wuhan 430062, People's Republic of China