

Adsorption of copper ions from aqueous solution by citric acid modified soybean straw

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Abstract

The objectives of the present study were to convert soybean straw to a metal ion adsorbent and further to investigate the potential of using the adsorbent for the removal of Cu^{2+} from aqueous solution. The soybean straw was water or base washed and citric acid (CA) modified to enhance its nature adsorption capacity. The morphological and chemical characteristics of the adsorbent were evaluated by spectroscopy and N_2 -adsorption techniques. The porous structure, as well as high amounts of introduced free carboxyl groups of CA modified soybean straw makes the adsorbent be good to retain Cu^{2+} . The adsorption capacities increased when the solution pH increased from 2 to 6 and reached the maximum value at pH 6 (0.64 mmol g^{-1} for the base washed, CA modified soybean straw (CA-BWSS)). The Cu^{2+} uptake increased and percentage adsorption of the Cu^{2+} decreased with the increase in initial Cu^{2+} concentration from 1 mM to 20 mM. Both the Langmuir and Freundlich adsorption isotherms were tested, and the Freundlich model fitted much better than the Langmuir model. It was found that CA-BWSS have the highest adsorption capacity of the four kinds of pretreated soybean straw.

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Keywords: Soybean straw; Citric acid; Copper; Adsorption isotherm; Low cost adsorbent

1. Introduction

Copper has been known as one of the most common toxic metals, which finds its way to the water stream from industries like electroplating, mining, electrical and electronics, iron and steel production, the non-ferrous metal industry, the printing and photographic industries and metalworking and finishing processes [1]. As with other heavy metals, copper in traces is necessary for life processes. However, with higher concentrations of this element in the environment and the consequent increase in human intake, copper concentrations have reached toxic levels causing various diseases and disorders such as liver damage, Wilson disease and insomnia [2]. According to U.S. Environmental Protection Agency (EPA) standards, the permissible limit of copper for industrial effluents to be discharged to surface water is 0.25 mg/L . Other countries also have stringent standards for Cu^{2+} effluent discharge. So, the removal of copper from industrial effluents is important before discharging them into aquatic environments or on to land.

Conventional methods for removing metals from industrial effluents include chemical precipitation, electrolysis, membrane separation, ion exchange, and adsorption by activated carbon. Most of these methods suffer from some drawback such as high capital or high operational cost or disposal of resulting sludge. In recent years, more and more interest has been directed to the investigation of low-cost materials such as agricultural by-products, industrial wastes and biological materials as adsorbents for the removal of heavy metal from industrial wastewater [3–5].

Agricultural by-products are high volume, low value and underutilized lignocellulosic biomaterials, and contain high levels of cellulose, hemicellulose and lignin [6]. However, adsorption capacity of crude agricultural by-products is low in general. Chemical modification has shown great promise in improving the adsorption and the cation exchange capacity of agricultural by-products [4,7–9]. Citric acid (CA) is a low cost material used extensively in the food industry. Wing [7] derivatized corn by-products with CA and observed considerable improvement in Cu^{2+} binding. When heated, CA will dehydrate to yield a reactive anhydride which can react with the sugar hydroxyl groups to form an ester linkage. The introduced free carboxyl groups of CA increase the net negative charge on the

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Nomenclature

b	energy related constant in Langmuir equation (L mmol^{-1})
BWSS	base washed soybean straw without further modification
C_0	the initial concentration of solute in solution (mmol L^{-1})
C_e	concentration of solute in solution (mmol L^{-1})
CA	citric acid
CA-BWSS	base washed, CA modified soybean straw
CA-WWSS	water washed, CA modified soybean straw
FESEM	field emission scanning electron microscope
FTIR	Fourier transform infrared
k_F	Ferundlich constant (mmol g^{-1})
n	Ferundlich constant
pK_a	acid dissociation constant
q_e	sorption capacity at equilibrium (mmol g^{-1})
Q_{\max}	the maximum sorption value (mmol g^{-1})
r^2	the correlation coefficient
rpm	revolution per minute
WWSS	water washed soybean straw without further modification

straw fiber, thereby increasing its binding potential for cationic contaminants [8,9–11].

Soybean straw is a lignocellulosic agricultural stalk. It's plentiful, inexpensive, and a renewable resource. Over 16 million metric tons of soybeans are produced annually in China [12], but most of soybean straw is arbitrarily discarded or set on fire. These disposals must result in resource loss and environmental pollution. The exploitation and utilization of soybean straw must bring obvious economic and social benefit to mankind.

The objective of this study was to modify soybean straw with CA after being washed with sodium hydroxide to enhance its ability to adsorb Cu^{2+} , then the adsorption process was investigated as a function of initial pH and concentration of Cu^{2+} . Furthermore, the mechanism of Cu^{2+} adsorption was studied by Fourier transform infrared (FTIR) analysis and the effect of washing or CA modification was assessed.

2. Materials and methods

2.1. Adsorbent preparation

Raw soybean straw was obtained from a farm in Weifang City Shandong Province. After removing the leaves and pods, the collected biomaterial was cut into segment of 10 cm length and washed with water to remove soil and dust, and then dried in an oven at 50°C until constant weight. Dried straw segment was milled and sieved to retain the 0.15–0.38 mm (40–100 mesh) fraction for further pretreatments.

The sieved straw was water washed or base washed by stirring 200 g sieved straw in 2 L of deionised water or 4 L of 0.1 M NaOH respectively. Both of the slurries were stirred at

500 rpm for 1 h at 20°C . Then the slurries were poured onto a 100 mesh sieve and rinsed with deionised water. This procedure was repeated two times for water washed soybean straw (WWSS). As for base washed soybean straw (BWSS), the procedure was repeated two more times to ensure removal of base from the straw. The water washed or base washed straw was then dried overnight at 50°C .

The chemical modification of soybean straw was made according to the similar method previously described by Vaughan et al. [10]. Water washed (WW) or base washed (BW) straw was mixed with 0.6 M CA at a ratio of 1.0 g straw to 10 mL CA. After being stirred at 500 rpm for 30 min at 20°C , both of the acid straw slurries were placed in a stainless steel tray and dried at 50°C in a forced air oven. After 24 h, the thermochemical reaction between acid and straw was proceeded by raising the oven temperature to 120°C for 90 min. After cooling, the reacted products were washed with 200 mL deionised water per gram of products to remove any excess of CA. This volume of water was sufficient to remove unreacted CA since no turbidity from lead (II) citrate was observed when the washed straw was suspended in 10 mL of water to which 10 mL of 0.1 M lead (II) nitrate was added. Lastly, both the water washed, citric acid modified soybean straw (CA-WWSS) and base washed, citric acid modified soybean (CA-BWSS) were dried at 50°C until constant weight and preserved in a desiccator as adsorbent for further use.

2.2. Adsorbent characterization

The morphological characteristics of soybean straw were observed by using a field emission scanning electron microscope (FESEM, FEI Sirion 200). The acceleration voltage (Acc.V) was 5.0 kV, and the spot size (SE) was 4.0. The textural characteristics like surface area (BET method) and pore size distribution (MP method for micropores (<2 nm) and BJH method for mesopores (2–200 nm)) were all determined using N_2 -adsorption techniques (BELSORP-mini, Japan, Inc.). The functional groups present in the adsorbent were characterized by a Fourier transform infrared (FTIR) spectrophotometer (Bruker, Equinox 55), using KBr discs to prepare the soybean straw samples.

2.3. Solution preparation

Copper solution was prepared by dissolving solid $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in deionised water. Diluted HNO_3 and NaOH solutions were used for pH adjustment. All chemicals used in this work were purchased as reagent grade from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). In all experimental work, deionised water was used.

2.4. Cu^{2+} adsorption experiments

Batch experiments were carried out at room temperature ($20 \pm 2^\circ\text{C}$) in stoppered conical flasks by shaking a fixed mass of 0.5 g of dry soybean straw adsorbents, with 50 mL of Cu^{2+} solution at 250 rpm until equilibrium was reached. The initial

pH values of the solution were previously adjusted with dilute HNO_3 or NaOH using pH meter.

In order to ascertain the contact time that was necessary to achieve the equilibrium state (characterized by unchanging Cu^{2+} concentration in the solution), simple preliminary sorption-kinetic experiments were performed stirring in different conical flasks 0.5 g of dry soybean straw adsorbents with 50 mL of 15 mM of Cu^{2+} solution at initial pH around 5. Samples were withdrawn at pre-determined time intervals.

After agitation, samples were withdrawn from each flask and about 25 mL of the Cu^{2+} solution was separated from the adsorbent by filtration for analysis. The initial and final concentration of Cu^{2+} were determined by inductively coupled plasma atomic

emission spectrophotometry (Iris Advantage 1000). The wavelength was 324.754 nm for copper analysis.

The measured Cu^{2+} concentrations were then used to calculate the adsorption capacity, q_e (mol g^{-1} or mmol g^{-1}) of the adsorbent using the following mass balance equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

The percentage of Cu^{2+} adsorbed on the adsorbent was calculated by the following equation:

$$p_e (\%) = \frac{100(C_0 - C_e)}{C_0} \quad (2)$$

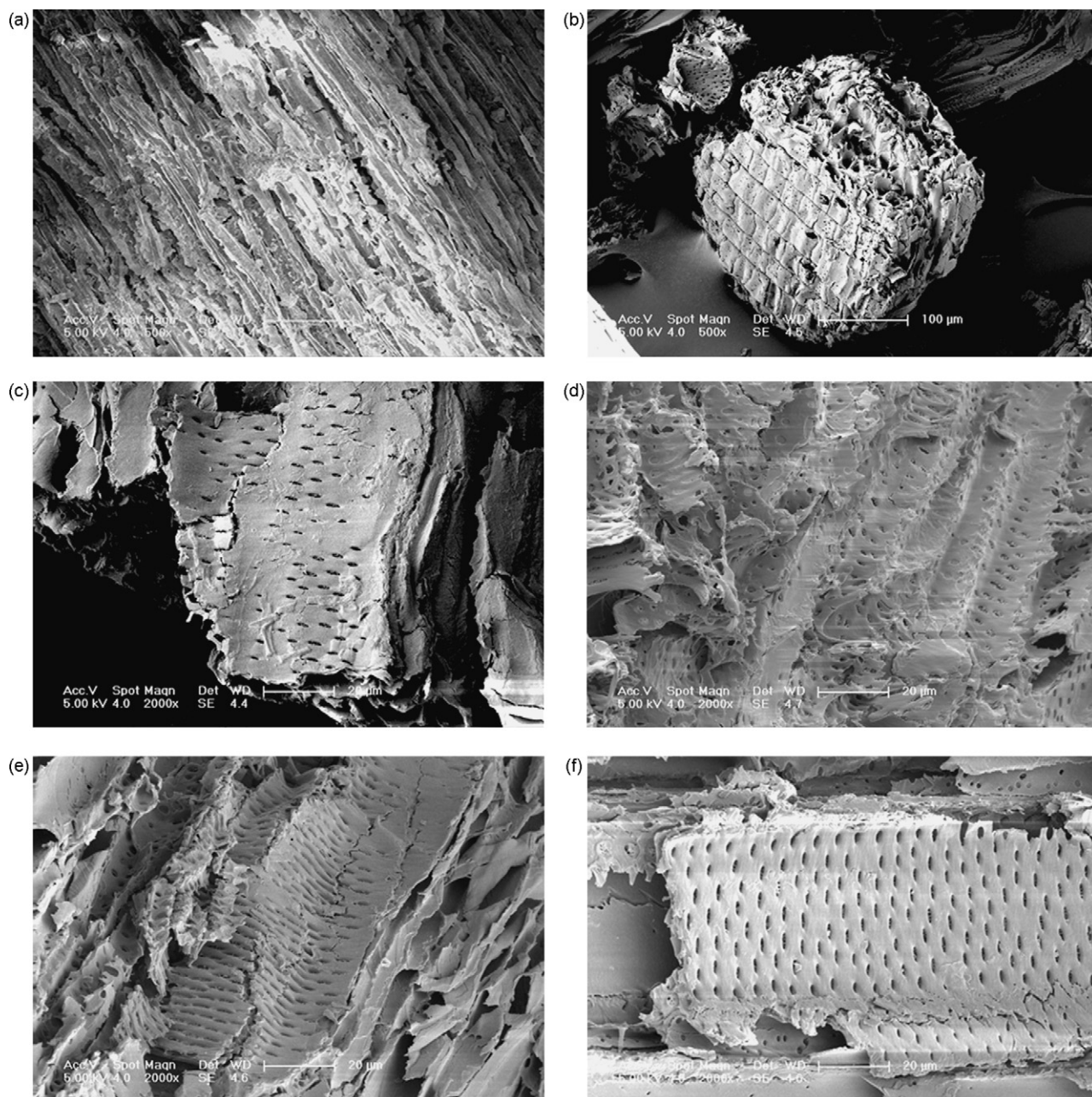


Fig. 1. FESEM micrographs of soybean straw before and after CA modification: (a) raw, (b) milled, (c) water washed, (d) base washed, (e) water washed, CA modified (f) base washed, CA modified.

where C_0 , C_e , V , and m are initial Cu^{2+} concentration (mmol L^{-1} or mM), Cu^{2+} concentration at equilibrium (mmol L^{-1} or mM), the volume (L) of the solution and weight (g) of adsorbent, respectively.

The experiments were conducted in duplicate and the negative controls (with no adsorbent) were simultaneously carried out to ensure that adsorption was by adsorbents and not by the container.

3. Results and discussion

3.1. Adsorbent characterization

Like all agriculture biomass, the highly anisotropic cellular structure gives the soybean straw porous tissue skeleton ranging from nanometers to micrometers. Fig. 1 shows the FESEM micrographs for the soybean straw samples before and after CA modification. Both of the samples are clearly porous, and there are pores of varying sizes within the particles. The raw sample exhibited rigid and highly ordered fibrils (Fig. 1a). The fibers of milled and sieved sample appeared to be separated from the initial connected structure and fully exposed (Fig. 1b and c). This increased the external surface area and the porosity of the materials. Fig. 1d, e and f shows the FESEM micrographs for the

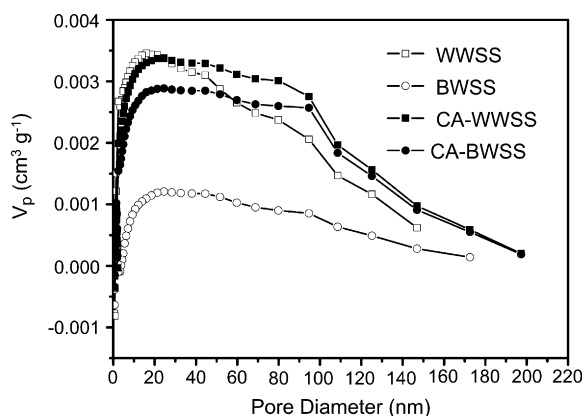


Fig. 2. Pore size distribution (MP method for 1–2 nm and BJH method for 2–200 nm).

Table 1
Chemical composition of soybean straw

Ingredient	wt.%
Lignin	16
Cellulose	38
Hemicellulose	16
Nitrogen	0.832
Ash	6

All data on a dry matter basis [13].

soybean straw samples after chemical modification. Comparison of the micrographs revealed that modification did not significantly change the morphology of the straw surface structure. The morphology of this material can facilitate the adsorption of metals, due to the irregular surface of the soybean straw, thus makes possible the adsorption of metals in different parts of this material.

Fig. 2 shows the pore size distribution of the soybean straw using N_2 -adsorption techniques. It was noted that there are few micropores in the structure of all the soybean straw samples. In addition to FESEM micrographs, it is evident from Fig. 2 that all soybean straw adsorbents are mainly mesoporous (2–100 nm). The BET surface areas of soybean straw are very low, $0.66 \text{ m}^2 \text{ g}^{-1}$ for the unmodified soybean straw, and become much lower after chemical modification. It might suggest that some large pores became clogged by CA molecules after chemical modification.

The chemical composition of original soybean straw is shown in Table 1 [13]. In the soybean straw cellulose and lignin take up to 54% of the dry weight. In contrast to hemicellulose that is easily hydrolyzed by dilute acid or base, both of cellulose and lignin are strong and resistant to hydrolysis. So, after base washing, the remnant cellulose and lignin can react with CA during modification. The CA modification is schematically expressed in Fig. 3. The cellulosic hydroxyl groups combined with citric acid anhydride to form an ester linkage and introduced carboxyl groups to the straw fiber. The mechanism could be further confirmed by the FTIR spectra.

The FTIR spectra of the soybean straw samples are shown in Fig. 4. As indicated in all the samples, the peaks observed at 2930 cm^{-1} can be assigned to the C–H group, and the

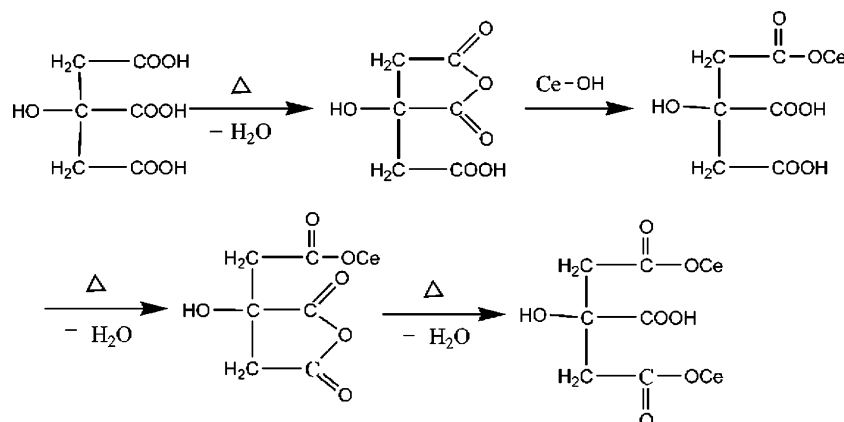


Fig. 3. Thermochemical reaction of soybean straw cellulose and citric acid.

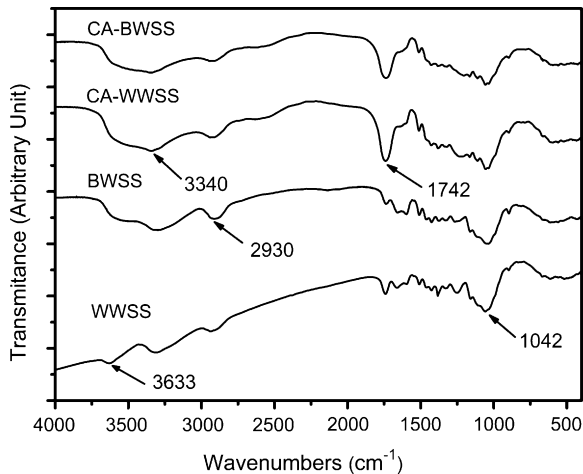


Fig. 4. FTIR spectra of soybean straw adsorbents.

peaks around 1042 cm^{-1} are characteristics of C–O group of primary hydroxyl stretching that may be attributed to cellulose structure of the soybean straw. Comparing with the IR spectrum of samples not CA modified, it could be seen that there was a strong characteristic stretching vibration adsorption band of carboxyl group at 1742 cm^{-1} in IR spectrum of CA modified soybean straw samples. It reflected the result of citric acid esterification [11]. The broad adsorption peaks around 3340 cm^{-1} also confirms the existence of carboxylic O–H groups ($2500\text{--}3500\text{ cm}^{-1}$) after CA modification.

So, based on the porous structure and the irregular surface, as well as high amounts of introduced free carboxyl groups, it can be concluded that CA modified soybean straw presents an adequate physical and chemical characteristics to adsorb metal ions.

3.2. Effect of contact time

The adsorption of Cu^{2+} from a solution of 15 mM by soybean straw adsorbents versus contact time is shown in Fig. 5. It can be seen that the adsorption rates of Cu^{2+} were very rapid during

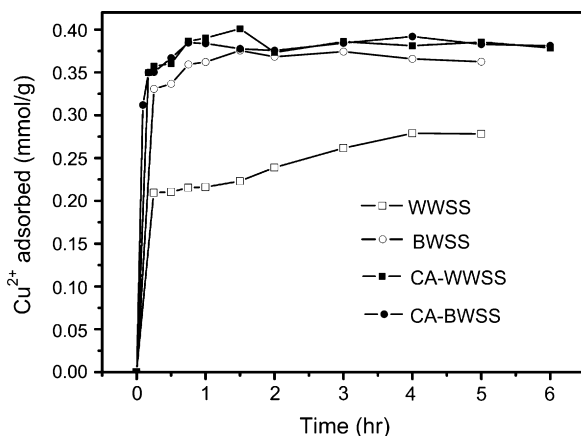


Fig. 5. Effect of contacting time on Cu^{2+} adsorption (0.5 g adsorbent, 50 mL of 15 mM Cu^{2+} solution, initial pH 5, $20 \pm 2^\circ\text{C}$).

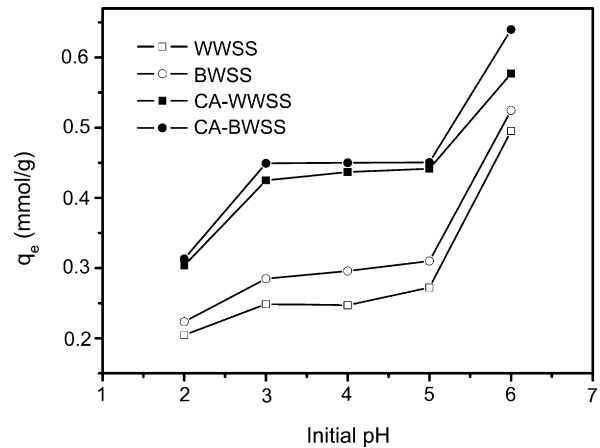


Fig. 6. Effect of initial pH on Cu^{2+} adsorption (0.5 g adsorbent, 50 mL of 20 mM Cu^{2+} solution, $20 \pm 2^\circ\text{C}$ for 24 h).

the first 10 min. After a very rapid adsorption, the adsorption rates of Cu^{2+} slowly declined. Initially, the adsorption sites are open and the metal ions interacts easily with the sites and hence a higher rate of adsorption is observed. Further, the driving force for adsorption – the concentration difference between the bulk solution and the solid–liquid interface – is higher initially and this results a higher adsorption rate. However, after the initial period, slow adsorption may be due to slower diffusion of solute into the interior of the adsorbent [14].

For all the samples except WWSS, within one hour the Cu^{2+} adsorption achieved equilibrium and the curve became flattened. For WWSS, the equilibrium was attained after four hours, a much longer time. However, for experimental convenience and to ensure equilibrium, a shaking time of 24 h was used in all further sorption experiments. Other authors using agriculture by-products and biomass wastes found similar sorption kinetics [14–16]. The rapid metal removal has significant practical importance, as this will facilitate the use of small adsorbent volumes to ensure efficiency and economy [5].

3.3. Effect of initial pH

The influences of the initial pH of Cu^{2+} solution were investigated over a range from 2 to 6. The experiments were carried out at pH values below the pH where copper hydroxide chemical precipitation occurs, which has been estimated as $\text{pH} > 6.3$ for $\text{Cu}(\text{OH})_2(\text{s})$ [5]. In order to avoid addition of strange ions, when the initial pH of Cu^{2+} solution was adjusted to the desired value no efforts were made to maintain the solution pH while Cu^{2+} was being adsorbed.

As elucidated in Fig. 6, for all the samples, the Cu^{2+} adsorption capacities were minimum at the initial pH 2. For the samples without CA modification, its main functional group is hydroxyl group. Along with increase of pH value, the concentration of H^+ ions that compete with Cu^{2+} for the adsorption sites decreased, the amount of Cu^{2+} absorbed on WWSS and BWSS gradually increased as the initial pH was increased from pH 2 to pH 5. For CA modified samples, its practical functional group is carboxyl

Table 2
Unmodified/modified agricultural waste utilized for removal of Cu^{2+} by adsorption

Adsorbent	Adsorbent dose (g/L)	C_0 (mg/L)	Optimum pH	Adsorption capacity (mg/g)	References
Grape stalks wastes	10	10	5.5	0.78	[5]
Citric acid modified soybean hulls	10	1271	NA	154.90	[8]
Dehydrated wheat bran	1	100	5.0	45.00	[17]
Wheat shell	12	250	5.0	10.84	[21]
Activated poplar sawdust	5	50	5.0	9.24	[22]
Tartaric acid modified rice husk	5	100	5.2	17.20	[23]
Teak leaves powder	3.3	100	5.5	13.14	[24]
Cocoa shells	5	15.88	2.0	2.87	[25]
Orange peel	1	25	6.0–8.0	3.65	[26]
Banana peel	1	25	6.0–8.0	4.75	[26]
Peanut hulls	10	32	NA	10.17	[27]
Peanut hulls pellets	10	32	NA	9.11	[27]
Cassava waste	NA	63.5	4.0–5.0	56.82	[28]
Coirpith	9	126	4.0–5.0	10.22	[29]
CA-BWSS	10	1271	5.0	28.60	Present study

NA: not available.

group and the pK_a value of carboxyl group is about 3. When $\text{pH} < 3$, the non-ionic form of carboxyl group, $-\text{COOH}$, was presented, Cu^{2+} adsorption was small because of the absence of electrostatic interaction. When $\text{pH} > 3$, carboxyl group is turned into $-\text{COO}^-$, Cu^{2+} adsorption is increased obviously and a plateau was reached at around $\text{pH} 3.0\text{--}5.0$ [11]. However, for all the samples, the Cu^{2+} removal percentage is significantly altered beyond $\text{pH} 5$ and reached maximum at the initial pH of 6. A similar observation was found in the adsorption of Cu^{2+} by dehydrated wheat bran [17]. This may be due to the fact that pH strongly influence not only the active sites on the surface of adsorbent, but also the speciation and the biosorption availability of the heavy metals. The metal cations in aqueous solution convert to different hydrolysis products. At low to high pH values, copper ions exist as Cu^{2+} , $\text{Cu}(\text{OH})^+$ and $\text{Cu}(\text{OH})_2$. The dominant species of copper in the range 3–5 of pH are Cu^{2+} and $\text{Cu}(\text{OH})^+$, while the copper at above 6.3 occurs as insoluble $\text{Cu}(\text{OH})_2(\text{s})$ [18,19]. At $\text{pH} 6$, there is a very small quantity of Cu^{2+} , but a large quantities of $\text{Cu}(\text{OH})^+$ and $\text{Cu}(\text{OH})_2$ [20]. So, the sharp increase in the range 5–6 of pH can be explained by precipitating copper ions in solution. In this study, these copper cations at around $\text{pH} 5.0$ would be expected to interact more strongly with the negatively charged binding sites in the soybean straw adsorbents. As a result, the optimum pH for Cu^{2+} adsorption was found as 5.0 and the other adsorption experiments were performed at this pH value.

The effect of pH on the adsorption of Cu^{2+} has been investigated by various investigators using a variety of different adsorbents obtained from agricultural by-products. A comparison of the results of CA-BWSS obtained in this work with those of some other adsorbents reported in literature is given in Table 2. Generally, the optimum pH for the removal of Cu^{2+} is in the range 5–6: dehydrated wheat bran, wheat shell and activated poplar sawdust as the adsorbent all at $\text{pH} 5$ [17,21–22], tartaric acid modified rice husk as the adsorbent at $\text{pH} 5.2$ [23], grape stalks wastes and teak leaves powder as the adsorbent at $\text{pH} 5.5$ [5,24].

3.4. Effect of initial Cu^{2+} concentration

Several experiments were undertaken to study the effect of initial Cu^{2+} concentration on the Cu^{2+} removal from the solution. The results obtained are shown in Fig. 7. For all the samples, the data show that the metal uptake increases and percentage adsorption of the Cu^{2+} decreases with increase in initial Cu^{2+} concentration. For CA-BWSS, the percentage decrease is between 68.6% ($0.069 \text{ mmol g}^{-1}$) and 22.5% ($0.450 \text{ mmol g}^{-1}$) where the initial concentrations are increased between 1 and 20 mM. This is because at low ion concentrations the ratio of surface active sites to the total metal ions in the solution is high and hence all metal ions may interact with the adsorbent and be removed from the solution. However, at high concentrations, the driving force, i.e. concentration gradient is stronger, and the amount of Cu^{2+} adsorbed per unit weight of adsorbent, q_e , is higher. As a result, the soybean straw adsorbent is more efficient for the wastewaters of low ion concentrations, and the purification yield can be increased by diluting the wastewaters containing high metal ion concentrations [24].

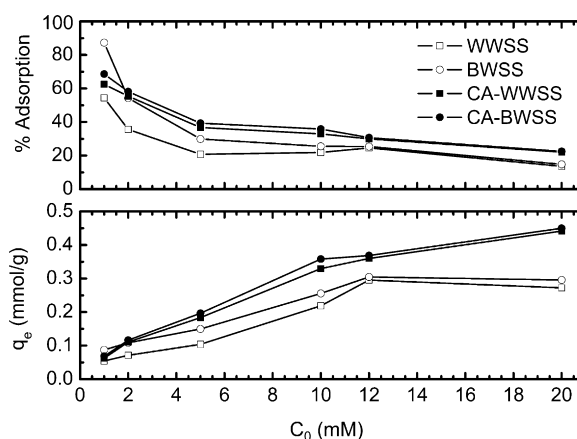


Fig. 7. Effect of initial Cu^{2+} concentration on Cu^{2+} adsorption (0.5 g adsorbent, 50 mL of Cu^{2+} solution, initial $\text{pH} 5$, $20 \pm 2^\circ\text{C}$ for 24 h).

3.5. Adsorption isotherms

Two of the most commonly used isotherm theories have been tested in this work, *i.e.*, the Langmuir and Freundlich equilibrium isotherm theories. The form of Langmuir equation can be represented by the following Eq. (3):

$$q_e = \frac{bQ_{\max}C_e}{1 + bC_e} \quad (3)$$

or in the linear form

$$\frac{C_e}{q_e} = \frac{1}{bQ_{\max}} + \frac{C_e}{Q_{\max}}, \quad (4)$$

where C_e is the equilibrium concentration of remaining metal in the solution (mmol L^{-1} or mM). q_e is the amount of a metal adsorbed per mass unit of adsorbent at equilibrium (mmol g^{-1}). Q_{\max} is the amount of adsorbate at complete monolayer coverage (mmol g^{-1}). b (L mmol^{-1}) is a constant that relates to the heat of adsorption.

Freundlich isotherm model has the following form [30–31]:

$$q_e = k_F C_e^n \quad (5)$$

or in the linear form

$$\log q_e = \log k_F + n \log C_e \quad (6)$$

where k_F ($\text{mmol}^{1-n} \text{g}^{-1} \text{L}^n$) represents the adsorption capacity when metal equilibrium concentration equals to 1, and n represents the degree of dependence of adsorption with equilibrium concentration.

Adsorption isotherms of copper ion adsorption by the four kinds of adsorbents are given in Fig. 8. In this study, the adsorption isotherms were generated at pH 5 with concentrations ranging from 1 to 30 mM and the adsorption data were described using the Langmuir and Freundlich isotherm models. The results of these analyses, using linear regression procedures, are shown in Table 3. The shape of all the isotherms is of “L1” type according to Giles classification for isotherms [32], which indicated that the curves do not reach any plateau (the adsorbents do not show clearly a limited adsorption capacity) [33]. L-isotherm type (or Langmuir isotherm type) is usually associated with ionic substrates (e.g., metal cations) adsorption with weak competition from the solvent molecules [32,34].

Table 3 indicates that Langmuir model gives poor presentations for Cu^{2+} adsorption behavior by the unmodified soybean straw ($r^2 = 0.5973$ and 0.6877 for WWSS and BWSS, respectively). There is a slight deviation from linearity using the

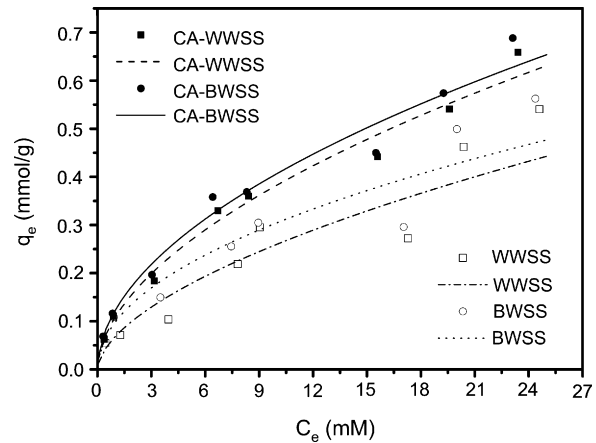


Fig. 8. Freundlich isotherms of Cu^{2+} at room temperature ($20 \pm 2^\circ\text{C}$). The adsorption isotherms were generated at pH 5 with concentrations ranging from 1 to 30 mM.

Langmuir isotherm model for describing Cu^{2+} adsorption by CA-modified soybean straw ($r^2 = 0.9058$ and 0.8969 for CA-WWSS and CA-BWSS, respectively).

Comparatively, Freundlich isotherm model gives better descriptions for Cu^{2+} adsorption data of all the four adsorbents, especially for the data of modified adsorbents ($r^2 = 0.9914$ and 0.9895 for CA-WWSS and CA-BWSS, respectively).

Freundlich parameters (k_F and n) indicate whether the nature of adsorption is either favorable or unfavorable [35]. The intercept is an indicator of adsorption capacity and the slope is an indicator of adsorption intensity. A high value of the intercept, k_F , is indicative of a high adsorption capacity [36]. A relatively slight slope $n \ll 1$ indicates that adsorption intensity is good (or favorable) over the entire range of concentrations studied, while a steep slope ($n > 1$) means that adsorption intensity is good (or favorable) at high concentrations but much less at lower concentrations [35,36]. In the four adsorption systems, n values are all less than unity which indicates that adsorption intensity is good (or favorable) over the entire range of concentrations studied.

Since the k_F values, reported in Table 3, can be used to indicate the relative adsorption capacity of the adsorbents [37], the adsorption capacity for the Cu^{2+} can be estimated as: CA-BWSS > CA-WWSS > BWSS > WWSS. Using the Langmuir model, the maximum adsorption capacity of the CA-modified soybean straw for Cu^{2+} can be estimated as: 0.76 mmol g^{-1} or 48.14 mg g^{-1} of CA-WWSS, 0.77 mmol g^{-1} or 48.81 mg g^{-1} of CA-BWSS.

Table 3
Langmuir and Freundlich model parameters (room temperature, 24 h, 50 mL solution, 5 g adsorbents)

Adsorbent	Langmuir plot		Freundlich plot			
	b (L mmol^{-1})	Q_{\max} (mmol g^{-1})	r^2	k_F	n	r^2
WWSS	0.0716	0.6923	0.5973	0.0683	0.5809	0.9245
BWSS	0.0943	0.6762	0.6877	0.0990	0.4882	0.9048
CA-WWSS	0.1338	0.7575	0.9058	0.1093	0.5447	0.9914
CA-BWSS	0.1504	0.7680	0.8969	0.1236	0.5174	0.9895

Note: Unit of k_F is $\text{mmol}^{1-n} \text{g}^{-1} \text{L}^n$.

3.6. Effect of wash types or modification

From Figs. 6–8, the curves indicate that CA-BWSS performed slightly better than CA-WWSS in Cu^{2+} adsorption tests, both CA-WWSS and CA-BWSS exhibited significantly higher adsorption than the unmodified soybean straw either water washed or base washed. Water washed soybean straw without modification adsorbed the least amount of Cu^{2+} . CA modification apparently increased the Cu^{2+} adsorption through ester formation of the sugars in the soybean straw. Although the modification process requires extra operational cost due to the consumption of CA, the improved adsorption capacities of the adsorbents may compensate for the cost.

The purpose of the washings was to remove water soluble surface debris or in the case of base washing, base soluble material on the soybean straw surface that might have interfered with the soybean straw adsorptive properties. A quantitative observation was noted that CA-BWSS and BWSS do not discolor Cu^{2+} solutions when used in batch assays for Cu^{2+} adsorption. CA-WWSS and WWSS leach a light brown or tan pigment into solution during the assay. The pigment changes the blue copper nitrate solution to green during the 24 h contact period. Other authors using soybean hulls for Cu^{2+} adsorption found the similar phenomena [8]. This occurrence is undesirable because the adsorbent removes metal ions but adds organic constituents (pigment) that would require additional removal. Certainly, the end-user would prefer a clean, non-polluting product where any colorants produced were handled at the manufacturing stage. Therefore, if CA-modified soybean straw was used for the decontamination of metal-containing effluents, base treatment before CA modification is recommended.

4. Conclusions

The amount of Cu^{2+} adsorbed by soybean straw was increased by modification with CA, regardless of whether the samples were base washed or water washed. This is due to the increase in carboxyl groups imparted onto the straw by reaction with CA. However, of the four kinds of soybean straw samples, CA-BWSS had the highest Cu^{2+} adsorption. The adsorption capacities increased when the solution pH increased from 2 to 6 and reached the maximum value at pH 6 (0.50, 0.52, 0.58 and 0.64 mmol g^{-1} for WWSS, BWSS, CA-WWSS and CA-BWSS, respectively). The Cu^{2+} uptake increased and percentage adsorption of the Cu^{2+} decreased with the increase in initial Cu^{2+} concentration from 1 mM to 20 mM. The Freundlich isotherm fitted the experimental data much better than the Langmuir model, but for the two kind of CA modified soybean straw, there was only a slight deviation from linearity of Langmuir model. Consequently, using the Langmuir model, the maximum adsorption capacity of the CA-modified soybean straw for Cu^{2+} can be estimated as: 0.76 mmol g^{-1} for CA-WWSS, 0.77 mmol g^{-1} for CA-BWSS. However, further work should include performing experiments to study the effect of temperature and the thermodynamics, more detailed kinetics, adsorbent regeneration and the ultimate fate of heavy metals once removed from the adsorbent.

Finally, we can conclude that base washed, CA modified soybean straw may be used as an low cost alternate adsorbent for the decontamination of metal-containing effluents.

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