

Citric Acid Functionalizing Wheat Straw as Sorbent for Copper Removal from Aqueous Solution

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A cationic sorbent, which bears carboxyl groups of citric acid (CA) derived from esterified wheat straw, was prepared using the solid-phase esterifying technique. Copper (Cu) removal from aqueous solution with modified wheat straw (MWS) was investigated to evaluate its capacities of cation exchange and metal chelation. The effects of various experimental parameters (*e.g.*, solution pH, Cu concentration, sorbent dose, contact time, and presence of light metal) are studied in batch experiments. The maximum value of Cu removal appeared in the range of pH 4 to 5. The percentage of Cu removal decreased with increasing initial Cu concentration. The isothermal data of Cu sorption conformed well to the Langmuir model, and the maximum sorption capacity (Q_m) of MWS for Cu was 78.13 mg/g. For 100 mg/l of Cu solution, a removal ratio of greater than 96% could be achieved with 2.0 g/l or more of MWS. The equilibrium of Cu removal was reached within 90 min. The presence of univalent and bivalent light metal ions (Na⁺, K⁺, Mg²⁺, and Ca²⁺) did not significantly interfere with Cu removal by MWS.

Key words — removal, copper, citric acid, modification, wheat straw

INTRODUCTION

Heavy metal contamination is a main source of water pollution. The removal and recovery of heavy metals from wastewater are important in protecting the environment and human health. A number of techniques such as chemical precipitation, solvent extraction, electro dialysis, evaporation, membrane separation, reverse osmosis, ion exchange, and sorption have been employed to remove heavy metals from wastewater. However, strict environmental protection legislation, public environmental concerns, and the expense of conventional disposal methods provide incentives for developing novel techniques for heavy metal wastewater treatment.

Copper (Cu), a widely used metal in industry, is an essential trace element for human health and plays an important role in carbohydrate and lipid metabolism and in the maintenance of heart and blood vessel activity.¹⁾ The adult human body contains 100–150 mg of Cu, but excess amounts in the body can be toxic. The use of biomaterials for removing heavy metals from contaminated wastewater

has emerged as a potential alternative method to conventional techniques.²⁾ Many types of low-cost agricultural waste, such as apple waste,³⁾ peanut hull pellet,⁴⁾ olive pomace,⁵⁾ banana pith,⁶⁾ sawdust,⁷⁾ wheat shell,⁸⁾ wheat bran,⁹⁾ carrot residue,¹⁰⁾ sugar beet pulp,¹¹⁾ oil-palm fiber,¹²⁾ mustard oil cake,¹³⁾ and grape stalk waste,¹⁴⁾ have been used as sorbents for heavy metal removal from wastewater in recent years. For improving the physicochemical properties or sorption capacity of agricultural waste, various chemical modifications were employed.^{15–20)}

Wheat straw is a lignocellulosic agricultural waste containing about 35–40% cellulose, 20–30% hemicellulose, and 8–15% lignin. In China, over 110 million tons of wheat straw are produced annually.²¹⁾ In addition to its use as fuel or feed, large amounts of redundant wheat straw must be disposed of every year. In this study, citric acid esterified wheat straw was utilized as a cationic sorbent for the removal of Cu from aqueous solution in a batch system. The purpose of this study was to develop a new economic technique for wheat straw exploitation and utilization and to enhance the treatment of industrial wastewater and reduce the cost of wastewater treatment.

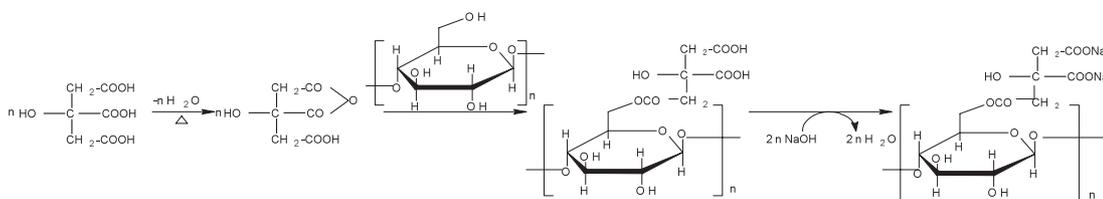
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MATERIALS AND METHODS

Modification of Wheat Straw — Wheat straw, supplied by a local farm, was cut into pieces 10 cm in length, washed with tap water to remove soil and dust, and then dried overnight at 50°C. Dried wheat straw segments are ground and sieved to retain the 20–40 mesh fractions for further chemical modification.

The chemical modification of wheat straw was carried out according to the method reported in the literature:²²⁾ Ground wheat straw was mixed with 0.5 mol/l of citric acid (CA) at the ratio of 1 : 12 (straw : acid, w/v) and stirred for 30 min. The acid/straw slurry was dried at 50°C in a forced-air oven for 24 hr. Then the thermochemical reaction between acid and wheat straw was performed at 120°C for 90 min. After cooling to room temperature, the CA-modified wheat straw was extensively washed to neutral pH with distilled water and filtrated. The filtered residue was suspended in NaOH 0.1 mol/l at suitable ratios and stirred for 60 min, followed by washing thoroughly with distilled water to remove residual alkali. Then the wet CA-modified wheat straw was dried at 50°C until constant weight and preserved in a desiccator for further use as a sorbent.

The chemical modification of wheat straw can be schematically expressed as:



Preparation of Cu Solution — A stock solution of Cu(II) was prepared by dissolving an accurately weighed amount of analytical-grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Merck, Darmstadt, Germany) in distilled water to the concentration of 500 mg/l. All working solutions were obtained by diluting the Cu stock solution in accurate proportions to different initial concentrations (25–250 mg/l).

Removal Experiments — Removal experiments were carried out in a rotary shaker at 150 rpm and ambient temperature ($20 \pm 2^\circ\text{C}$) using 250-ml shaking flasks containing 100 ml of different concentrations and initial pH values of Cu solution. The initial pH values of the solution were previously adjusted with diluted HNO_3 or NaOH using a pH meter. Different doses of modified wheat straw (MWS) were added to each flask, and then the flasks were sealed to prevent a change in volume of the solution during the experiments. After shaking the flasks for predetermined time intervals, the samples were withdrawn from the flasks and filtered through a membrane filter (0.45 μm). The concentration of residual Cu in the filtrate was determined with flame atomic absorption spectrometry.

The experiments were conducted in triplicate and negative control (with no sorbent) experiments were simultaneously carried out to ensure that sorption was caused not by the container but by the sorbent.

RESULTS AND DISCUSSION

Effects of Initial Solution pH on Cu Removal

The amount of Cu removal as a function of initial pH is shown in Fig. 1. When pH was less than 2, the amount of Cu removal was almost undetectable. As pH increased, the amount of Cu removal increased, and the sharpest increase was observed between pH 2 and 3. The maximum value of Cu removal appeared in the range of pH 4 to 5. However, the precipitation of insoluble Cu hydroxide occurred at pH values greater than 5. Therefore pH 4.5 was selected for the subsequent experiments.

Influence of Initial Cu Concentration on its Removal

The influence of the initial Cu concentration on its removal by MWS is represented in Fig. 2. When the initial Cu concentration was varied from 25 to 250 mg/l, the percentage of Cu removal markedly decreased from 98.60% to 62.75% at the optimum pH. However, the absolute amount of Cu removal per unit mass of MWS significantly increased from 12.33 to 78.44 mg/g with increasing initial Cu concentration.

The Langmuir sorption isotherm equation was used to evaluate the applicability of Cu removal data in Fig. 2. The linear Langmuir equation was:

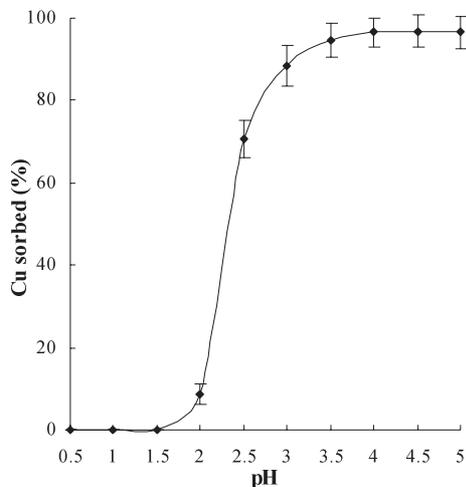


Fig. 1. Effect of Initial Solution pH on Cu Removal by MWS
Cu concentration, 100 mg/l; MWS dose, 2 g/l; contact time, 120 min.

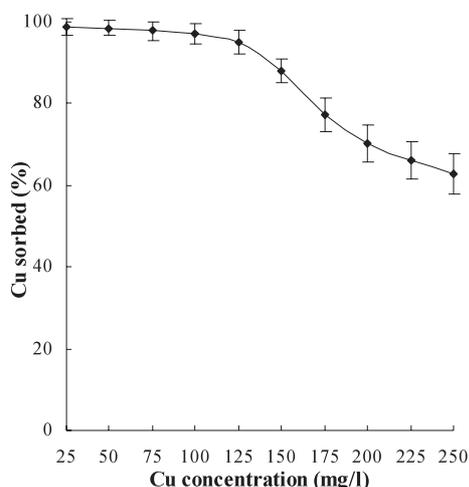


Fig. 2. Influence of Initial Cu Concentration on Its Removal by MWS
MWS dose, 2 g/l; contact time, 120 min; pH, 4.5.

$$C_e/q_e = 1/(aQ_m) + C_e/Q_m$$

where C_e (mg/l) is the concentration of the Cu solution at equilibrium, q_e (mg/g) is the amount of Cu sorbed at equilibrium, Q_m is the maximum sorption capacity and represents a practical limiting sorption capacity when the sorbent surface is fully covered with monolayer sorbate molecules, and a is the Langmuir constant. The Q_m and a values can be obtained from the slopes ($1/Q_m$) and intercepts ($1/aQ_m$) of linear plots of C_e/q_e versus C_e .

The Langmuir sorption isotherm of Cu sorbed on MWS is shown in Fig. 3. The experimental results indicated that the sorption isotherm of Cu sorbed on MWS followed the Langmuir model

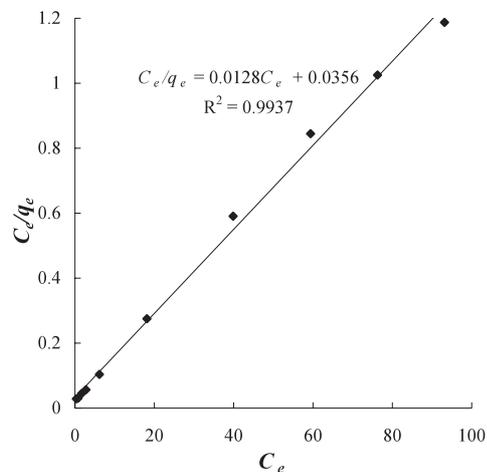


Fig. 3. Langmuir Plot for the Sorption of Cu by MWS

Table 1. Cu Sorption Capacities (Q_m) of Waste Biomaterials

Material	Q_m (mg/g)	Reference
MWS	78.13	Present study
Carrot residue	32.74	10
Modified rice husk	29	19
Sugar beet pulp	28.5	11
Wheat bran	14.5	9
Banana pith	13.5	6
Peanut hull pellet	12	4
Apple waste	10.8	3
Grape stalk waste	10.12	14
Sawdust	8.45	7
Wheat shell	8.34	8
Oil-palm fiber	1.98	12

($R^2 = 0.9937$) closely. The maximum sorption capacity (Q_m) of MWS for Cu was 78.13 mg/g. The maximum sorption capacities of some waste biomaterials for Cu are presented in Table 1. It appears that MWS has the greatest potential as a sorbent for Cu.

Effects of Sorbent Dosage on Cu Removal

The effects of sorbent dose on Cu removal by MWS are shown in Fig. 4. As the sorbent dosage was increased from 0.5 to 2.0 g/l, the percentage of Cu removal increased from 40.63% to 96.84%. With more than 2.0 g/l of sorbent dose, the equilibrium of Cu removal was reached and the ratio of Cu removal remained stable. Therefore the sorbent dosage of 2.0 g/l was chosen for the subsequent experiments.

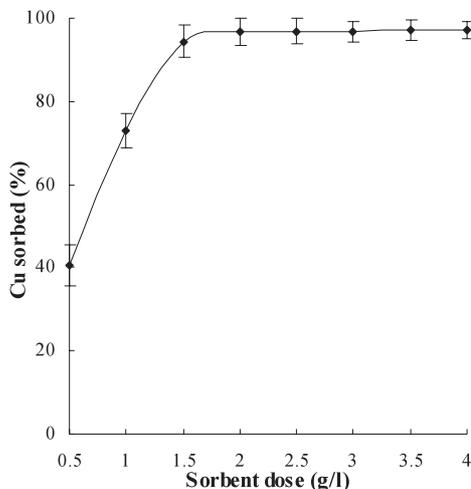


Fig. 4. Effects of Sorbent Dose on Cu Removal by MWS
Cu concentration, 100 mg/l; contact time, 120 min; pH, 4.5.

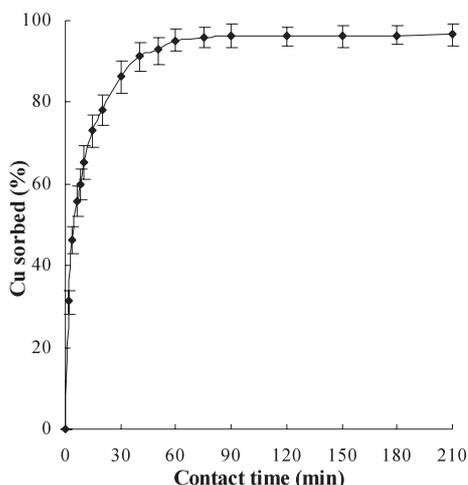


Fig. 5. Influence of Contact Time on Cu Removal by MWS
Cu concentration, 100 mg/l; MWS dose, 2 g/l; pH, 4.5.

Influence of Contact Time on Cu Removal

The influence of contact time on Cu removal by MWS is illustrated in Fig. 5. The rate of Cu removal was very rapid at the initial stage of sorption, caused by the fast diffusion and sorption of Cu ion onto the external surface of MWS. After that, the rate of Cu removal declined gradually and reached the equilibrium value at about 90 min. This process was controlled by the pore diffusion velocity of Cu ion into the intraparticle matrix of MWS.

Effect of the Presence of Light Metal Ion on Cu Removal

The effect of the presence of light metal ion (Na^+ , K^+ , Mg^{2+} , and Ca^{2+} , one at a time) on Cu

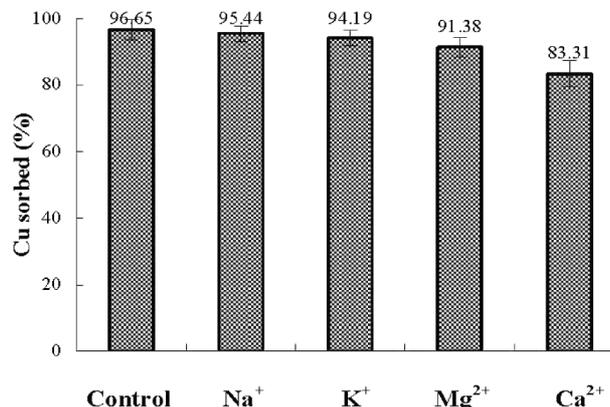


Fig. 6. Effects of Light Metal on Cu Removal by MWS
Cu concentration, 100 mg/l; MWS dose, 2 g/l; contact time, 120 min; pH, 4.5.

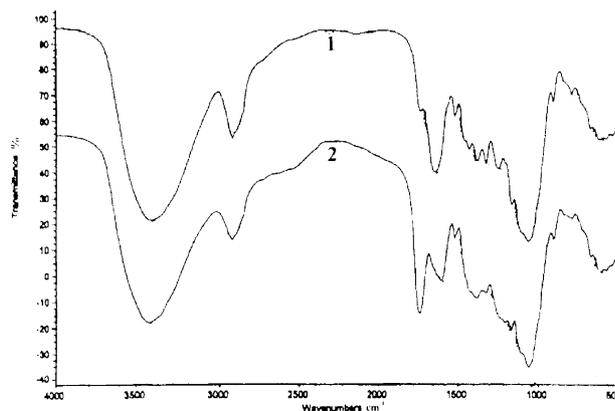


Fig. 7. IR Spectra of CWS and MWS (1: CWS; 2: MWS)

removal by MWS was investigated. The concentration of light metal ion used was 10 mmol/l. It can be seen from Fig. 6 that the effects of Na^+ on Cu removal by MWS are negligible, and K^+ , Mg^{2+} , and Ca^{2+} reduced the removal percentage by 2.46%, 5.27%, and 13.34%, respectively. These results indicate that light metal ion with more electric charge and larger atom radius have greater effects on Cu removal.

Analysis of IR Spectra

To judge whether citric acid was esterified into wheat straw, crude wheat straw (CWS) and MWS were subjected to Fourier transform infrared (FT-IR) spectroscopic analysis. The FT-IR spectra of samples were determined using the KBr translucent disk method with a FT-IR spectrometer (Nexus 870 FT-IR) over the wavelength region 4000–500 cm^{-1} . The FT-IR spectra of CWS and MWS are shown in Fig. 7. The two major changes in the FT-IR spec-

trum of MWS could be observed by comparing it with that of CWS: 1), a reduction in the hydroxyl (O—H) stretching band at 3417 cm^{-1} ; and 2), an obvious increase in the carbonyl (C=O) stretching vibration absorbance at 1737 cm^{-1} .

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