



Adsorption of Cu^{2+} from aqueous solution by modified biomass material

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Abstract: Cu^{2+} adsorption from simulated aqueous solution was investigated using a modified spent shiitake substrate (MSSS). The results showed that the MSSS has a high adsorption efficiency and removal performance. The Cu^{2+} removal rate of the MSSS reached above 95%. Compared with spent shiitake substrate (SSS), the specific surface area, electronegativity and surface functional groups of the MSSS were all improved, resulting in a high adsorption capacity. The Cu^{2+} adsorption of MSSS reached equilibrium after 0.75 h and was an exothermic reaction. The SEM and EDS analyses of the MSSS before and after Cu^{2+} adsorption showed that the pores on the surface of the MSSS were occupied after adsorption and the Cu content increased but the Na content decreased.

Key words: biomass material; spent shiitake substrate; modification; adsorption; heavy metal; Cu^{2+}

1 Introduction

Heavy metals as raw materials or catalysts are used widely in many industrial production, such as mining, metallurgy, electrolysis, electroplating and leather [1]. They can be subsequently released into the environment through wastewater, which has become a threat to human and local environment [2]. Because the heavy metals in water are difficult to be biodegraded and tend to accumulate in organisms through the food chain [3], the wastewater containing heavy metals should be treated before discharge. Beside heavy metal ions, the pH of mine water is between 3 and 4, due to a series of reactions of sulfide minerals in the presence of air, water and microorganisms.

Wastewater containing heavy metals is usually treated through neutralized sedimentation, precipitation with sulfides, redox, membrane separation, ion exchange, constructed wetlands and adsorption [4–7]. Among them, adsorption is a simple, inexpensive, effective and universal method [8]. Development and application of low-cost adsorption material have become the hotspot of current research [9–10]. Agricultural wastes have

recently attracted increasing interest from researchers because they are readily available and can be used as adsorbent for effectively removing heavy metals from wastewater [11–14].

Spent shiitake substrate (SSS) is the discarded bacteria stick from shiitake cultivation that is rich in dead fungal hyphae and cultivation materials, such as sawdust and bran [15]. Studies have shown that materials such as bran and sawdust adsorb heavy metals, thus SSS may be a suitable adsorbent [16–17]. TU et al [18] studied the performance of SSS in adsorbing lead ions and found that lead ions can be effectively adsorbed when the pH of wastewater ranged from 4.09 to 6.00 [18]. Nevertheless, our preliminary study indicated that the organic matter in SSS dissolves when it is directly used as an adsorbent, thereby increasing the chemical oxygen demand (COD) and chroma. Therefore, SSS needs to be modified before it can be used as an adsorbent.

Few studies have been conducted on SSS modification. To improve the performance of SSS and decrease the amount of organic matter dissolved during adsorption, which causes secondary pollution, SSS was modified via phosphate esterification supplemented with alkali and microwave treatment. The adsorption

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performance of SSS and the modified SSS (MSSS) was compared. MSSS was also used to treat simulated AMD at low pH and the underlying Cu^{2+} adsorption mechanism was studied.

2 Experimental

2.1 Materials

The SSS, provided by a company in Beijing, was dried at 80 °C to a constant mass, with a moisture content of 10%. The dried SSS was pulverized and filtered with a 850 μm screen. The SSS was placed in polyethylene bags and stored in a dryer.

2.2 Water sample

Simulated wastewater samples containing different concentrations of Cu^{2+} were prepared according to the condition of the AMD. The reagent used in the experiment was cupric sulfate. The pH of water samples was adjusted with H_2SO_4 (0.1 mol/L). All of the reagents used are analytically pure.

2.3 Modification of SSS

50 g of SSS was mixed with 750 mL of NaOH solution (mass fraction, 10%), and shaken for 2 h at 140 r/min and 30 °C, filtered and washed with deionized water until the pH of the washing fluid became neutral. The SSS was dried at 80 °C to a constant mass and placed in phosphoric acid solution (0.5 mol/L) with a solid-to-liquid ratio of 1:15. The SSS was heated in the microwave for 2.5 min, and then washed to remove the excess phosphoric acid solution. Finally, the resulting MSSS was dried at 80 °C to a constant mass, filtered with a 850 μm screen, placed in polyethylene bags and stored in a dryer.

2.4 Adsorption experiment

Water samples containing 150 mg/L of Cu^{2+} were prepared. The water samples in 500 mL flasks were mixed with 5 g of MSSS and rotated in a thermostated rotator (30 °C, 140 r/min) to achieve adsorption equilibrium. After adsorption, the materials were filtered. The Cu^{2+} concentration of the water sample was then measured. All the experiments were carried out in triplicate and some were repeated several times to establish the reproducibility of the results.

2.5 Analytical test

The Cu^{2+} concentration in the water sample was analyzed using atomic absorption spectrometry. The removal effectiveness was evaluated based on the adsorption quantity (q_t , mg/g) and removal rate (r , %), which were calculated by the following equations:

$$q_t = \frac{\rho_0 - \rho_t}{M} \quad (1)$$

$$r = \frac{\rho_0 - \rho_t}{\rho_0} \times 100\% \quad (2)$$

where ρ_0 represents the initial Cu^{2+} concentration; ρ_t represents the remaining Cu^{2+} concentration after adsorption (in mg/L); M represents the amount of adsorbent added (in g/L).

3 Results and discussion

3.1 SEM analysis of SSS and MSSS

The SEM micrographs of the SSS and MSSS are shown in Figs. 1(a) and (b), respectively. In Fig. 1(a), the surface of SSS is loose, with large pores and burrs on the surface. In Fig. 1(b), the cytoderm structure of the MSSS is damaged, with more small pores, greatly increasing its specific surface area. Furthermore, the pores are aligned. Greater specific surface areas are generally correlated with better adsorption performance. Therefore, the structure of MSSS is better for adsorption.

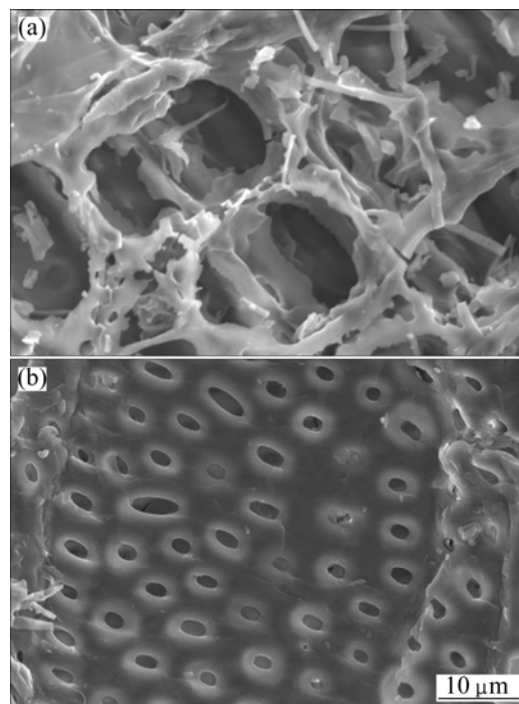


Fig. 1 SEM micrographs of SSS (a) and MSSS (b)

3.2 Zeta potentials of SSS and MSSS

The zeta potentials of the SSS and MSSS are shown in Fig. 2. Both the MSSS and SSS were negatively charged in the solution; thus, they can absorb Cu^{2+} through electrostatic attraction. The electronegativity of MSSS and SSS increased when pH increased, leading to the increase of adsorption capacity [19]. The electronegativity of MSSS was higher than that of SSS.

This result indicates that after modification, the negative charge on the surface increases, which is beneficial for Cu^{2+} adsorption.

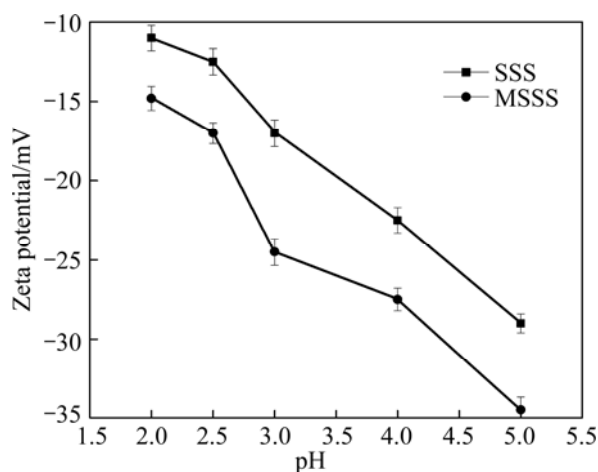


Fig. 2 Zeta potentials of SSS and MSSS

3.3 FTIR analyses of SSS and MSSS

The FTIR spectrograms of the MSSS and SSS were compared, as shown in Fig. 3. In the FTIR analysis of SSS, the strong peak near 3422.34 cm^{-1} is attributed to the stretching vibration of O—H, the peak near 2925.69 cm^{-1} is the antisymmetrical stretching vibration of $-\text{CH}_2$, the peak near 2362.81 cm^{-1} is probably the peak of CO_2 , the strong peak near 1633.71 cm^{-1} is the absorption band of amide II, the strong peak near 1321.70 cm^{-1} is the absorption band of amide III, the peak near 1051.29 cm^{-1} is the stretching vibration of C—OH and the peak near 786.83 cm^{-1} is the symmetrical stretching vibration of Si—O—Si [20].

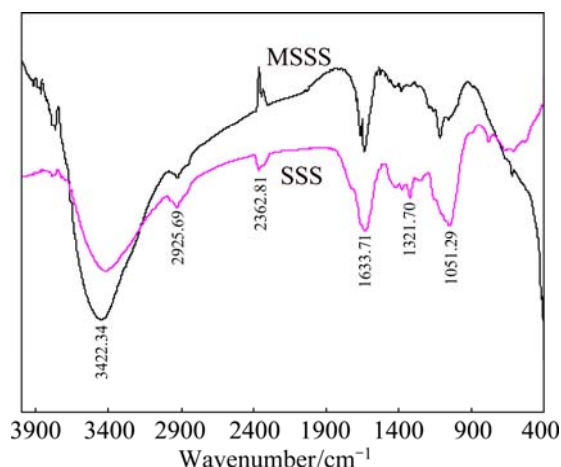


Fig. 3 FTIR spectrograms of MSSS and SSS

Comparison of the FTIR spectrograms of the MSSS and SSS revealed that the stretching vibration peak of O—H significantly changed. The peak was stronger and shifted from a wave number 3422.34 to 3450.64 cm^{-1} . This result strongly indicated that the modification of the

SSS increased the number of O—H. The absorption bands of amide II and III significantly changed. The peaks were thinner and shifted to 1641.15 and 1357.66 cm^{-1} , respectively. This result is attributed to phosphate esterification, a part of the $-\text{NH}_2$ in the amide molecules reacts with $-\text{POOH}$, and the phosphoryl group is formed. Finally, the stretching vibration peak of C—OH changed from 1051.29 cm^{-1} to 1113.98 cm^{-1} . The peak strength decreased because of the esterification reaction. According to the above analysis, phosphoric acid groups were successfully introduced through phosphate esterification supplemented with alkali and microwave treatment. Moreover, the number of hydroxide radicals increased and new functional groups, such as phosphoryl and ester groups were formed, which enhanced the adsorption capacity of MSSS.

3.4 Cu^{2+} adsorption experiment of MSSS under different pH values

The Cu^{2+} removal rate and the adsorption quantity of the MSSS at different pH values are shown in Fig. 4. The results showed that the Cu^{2+} removal rate and adsorption quantity of MSSS rapidly increased at pH values ranging from 0.7 to 3.0. The Cu^{2+} removal rate at pH 3.0 reached 86.99% and the adsorption quantity reached 13.05 mg/g . When pH increased to 4.8, the Cu^{2+} removal rate and the adsorption quantity both reached the highest values, 94.93% and 14.24 mg/g , respectively. These results indicated that MSSS reached adsorption saturation. The Cu^{2+} removal rate remained stable from pH 3 to 5.

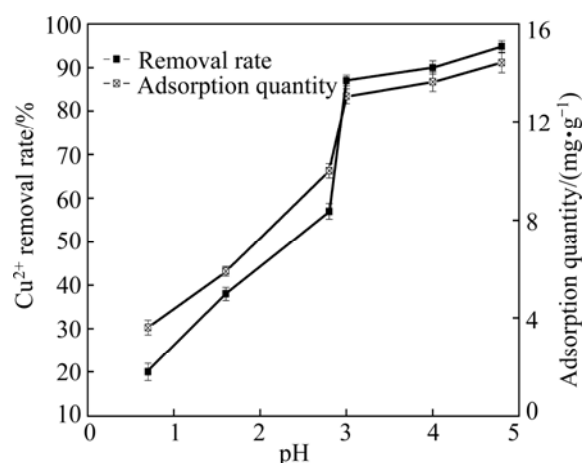


Fig. 4 Cu^{2+} removal rate and adsorption quantity of MSSS under different pH values

At pH 0.7, the Cu^{2+} removal rate of MSSS reached 19.66% and its adsorption quantity reached 2.95 mg/g . These results are significantly better than those of peanut shells, rice husks and so on [21,22]. Hence, MSSS can be applied in the treatment of wastewater at the low pH.

3.5 Adsorption time

The Cu^{2+} removal rate and adsorption quantity of the MSSS with different adsorption time are shown in Fig. 5. In the first 0.5 h of adsorption, the Cu^{2+} removal rate and adsorption quantity of the MSSS rapidly increased and reached 88.63% and 13.29 mg/g, respectively. When the reaction time exceeded 0.75 h, the Cu^{2+} removal rate and the adsorption capacity of the MSSS slowly increased and reached adsorption equilibrium, which is convenient for industrial application. If the copper ion concentration of the effluent is not lower than the standard value, the multistage series treatment can be used. Moreover, the MSSS which have been at sorption saturation can be combusted to recover the copper metal.

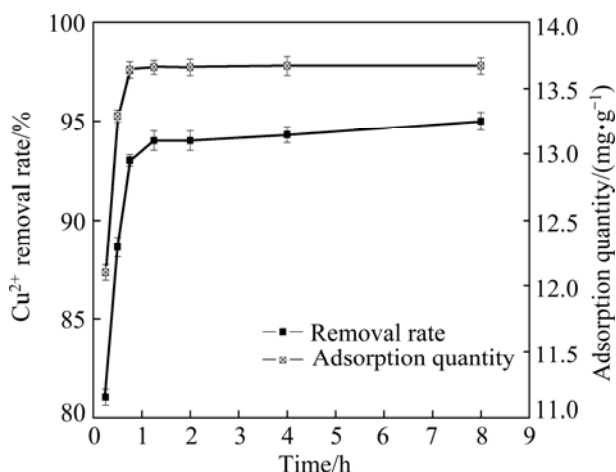


Fig. 5 Effect of adsorption time on Cu^{2+} removal

3.6 Adsorption thermodynamics

The Cu^{2+} adsorption quantity of the MSSS under different temperatures is shown in Fig. 6. The results showed that the Cu^{2+} adsorption quantity decreased with increasing temperature. However, when the temperature increased from 20 °C to 40 °C, the adsorption quantity of MSSS decreased by 1.98 mg/g, which indicates that temperature has minimal effect on the Cu^{2+} adsorption of the MSSS.

Studies on the adsorption thermodynamics achieved the regular trend, intensity, and driving force in the adsorption process. Therefore, calculating the adsorption experiment results by the variations of standard thermodynamic functions is a vital part in adsorption thermodynamics. The relationships among thermodynamic functions $\Delta G^\ominus$, $\Delta H^\ominus$, and $\Delta S^\ominus$, and equilibrium adsorption distribution coefficient K_d are shown as [23]:

$$\ln K_d = \frac{\Delta S^\ominus}{R} - \frac{\Delta H^\ominus}{RT} \quad (3)$$

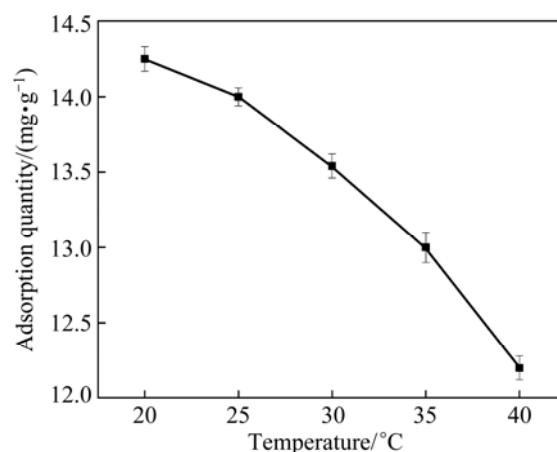


Fig. 6 Cu^{2+} adsorption quantity of MSSS under different temperatures

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus \quad (4)$$

$$\Delta G^\ominus = -RT \ln K_d \quad (5)$$

The equilibrium adsorption distribution coefficient K_d could be calculated using

$$K_d = \frac{\rho_0 - \rho_t}{\rho_t} \times \frac{V}{m} \quad (6)$$

where K_d is the equilibrium adsorption distribution coefficient, $\Delta G^\ominus$ is the standard free energy of adsorption, $\Delta H^\ominus$ is the standard adsorption enthalpy, $\Delta S^\ominus$ is the standard adsorption entropy change, R is the ideal gas constant, T is the temperature, V is the solution volume, and m is adsorbent dosage, ρ_0 is the initial Cu^{2+} concentration, ρ_t is the remaining Cu^{2+} concentration after adsorption.

K_d , $\Delta G^\ominus$, $\Delta H^\ominus$ and $\Delta S^\ominus$ were calculated based on MSSS adsorption thermodynamics experiment results of Cu^{2+} at different temperatures. The thermodynamics parameters for Cu^{2+} adsorption of the MSSS are shown in Table 1. The $\Delta G^\ominus$ was negative at temperatures ranging from 20 °C to 25 °C, which indicated that the adsorption was spontaneous. The $\Delta G^\ominus$ was positive at temperatures ranging from 30 °C to 40 °C, which indicates that the adsorption was not spontaneous beyond a certain temperature and external energy is needed to

Table 1 Thermodynamics parameters of MSSS for Cu^{2+} adsorption

$t/^\circ\text{C}$	$\Delta G^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta H^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta S^\ominus/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$
20	-1.12		
25	-0.49		
30	0.36	-0.052	-0.17
35	1.19		
40	2.30		

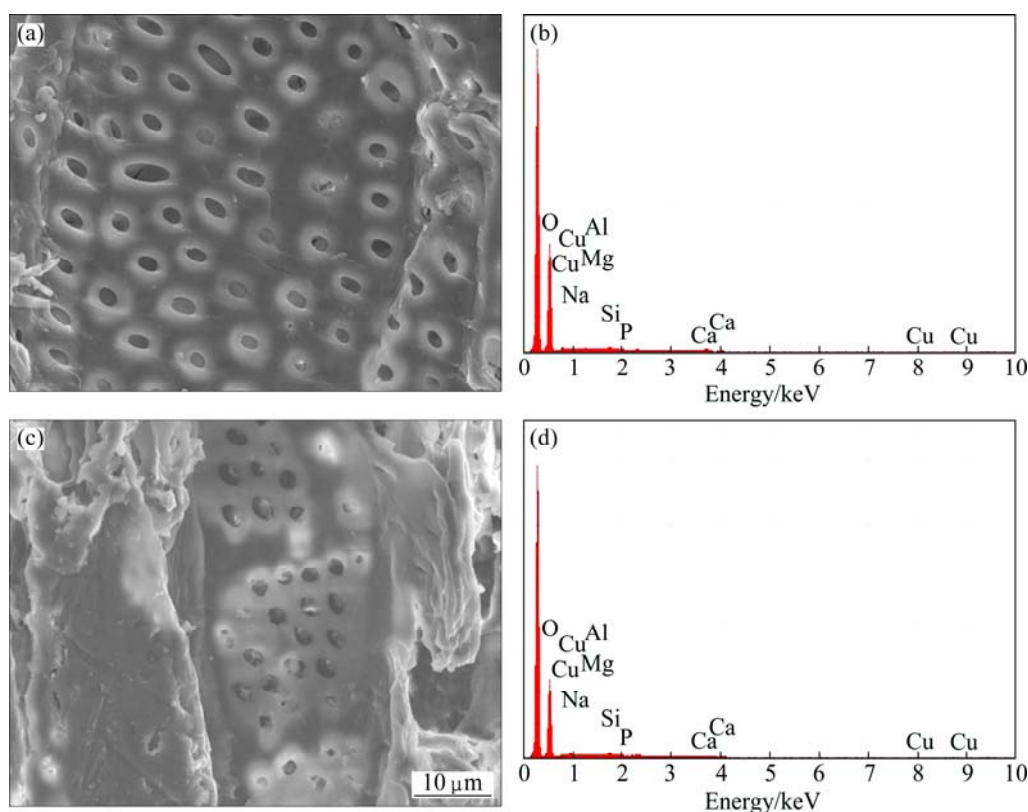


Fig. 7 SEM-EDS results of MSSS before and after Cu^{2+} adsorption: (a, b) Before adsorption; (c, d) After adsorption

reach the activation energy. The $\Delta H^\ominus$ and $\Delta S^\ominus$ remained negative across the whole temperature scope, which indicated that the adsorption was exothermic and the entropy of the adsorption process greatly reduced.

3.7 SEM-EDS analyses of MSSS before and after Cu^{2+} adsorption

The results of SEM-EDS analyses of MSSS before and after Cu^{2+} adsorption is shown in Fig. 7. After adsorption, the pores on the surface of MSSS were occupied. The MSSS contained C and O, as well as Na, Mg, Al, Si, P, Ca and Cu, before and after adsorption.

The results of the surface spectral analysis of MSSS before and after Cu^{2+} adsorption are shown in Table 2.

Table 2 Surface spectral analysis results of MSSS before and after Cu^{2+} adsorption

Element	Mass fraction/%		Mole fraction/%	
	Before	After	Before	After
Na	0.35	0.03	0.25	0.02
Mg	0.61	0.59	0.42	0.4
Ca	4.23	4.01	1.77	1.67
Al	0.56	0.94	0.35	0.58
Si	2.22	2.41	1.32	1.44
P	0.18	0.21	0.1	0.12
Cu	0.23	2.36	0.06	0.62

The contents of Na and Mg changed after adsorption, especially Na, which greatly decreased. Therefore, the Cu^{2+} adsorption by MSSS includes ion-exchange adsorption.

4 Conclusions

1) The MSSS obtained through the phosphate esterification with alkali treatment of the SSS has efficient adsorption performance and high removal efficiency of Cu^{2+} from wastewater containing heavy metal, even at a low pH. Cu^{2+} adsorption of MSSS reached equilibrium after 0.75 h.

2) The specific surface area and electronegativity of the MSSS were greater than those of the SSS. Furthermore, the number of hydroxide radicals increased and new functional groups, such as phosphoryl and ester groups formed on the surface of the MSSS. These results indicated that the modification improved adsorption capability of the MSSS.

3) The SEM and EDS analyses of the MSSS before and after Cu^{2+} adsorption showed that the pores on the surface of MSSS were occupied after adsorption, and the Cu content increased but the Na content decreased. The Cu^{2+} adsorption thermodynamics experiments showed that the Cu^{2+} removal by MSSS was exothermic and the entropy of the adsorption reduced greatly.

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改性生物质材料对水溶液中 Cu²⁺ 的吸附

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摘 要: 研究改性生物质材料——香菇培养基废料对水溶液中重金属铜离子的吸附性能。结果表明: 改性可以大大提高香菇培养基废料的吸附性能, 其铜离子去除率高达 95% 以上; 与天然香菇培养基废料相比, 改性后吸附材料的比表面积和电负性增大, 表面官能团数目及种类增多。在吸附 0.75 h 后, 改性香菇培养基废料对铜离子的吸附达到平衡, 该吸附过程是一个放热反应。改性香菇培养基废料吸附铜离子前后的扫描电镜和能谱分析表明, 吸附铜离子的材料表面可明显看到孔隙被占据, 且铜含量明显增加, 而钠含量减少。

关键词: 生物质材料; 香菇培养基废料; 改性; 吸附; 重金属; Cu²⁺

(Edited by Yun-bin HE)