

PAPER • OPEN ACCESS

Preparation and modification of biomass carbon and research of the adsorption of copper

To cite this article: Xiaohao Li and Yong Li 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **300** 052034

View the [article online](#) for updates and enhancements.



IOP | ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

Preparation and modification of biomass carbon and research of the adsorption of copper

Xiaohao Li *, Yong Li

Business School, Sichuan University, Chengdu, China

*Corresponding author e-mail: lixh0424@126.com

Abstract. With the acceleration of industrialization, industrial wastewater discharge makes environmental pollution more serious. How to deal with industrial wastewater has attracted more and more attention. It is a good method to deal with copper in wastewater by using biomass activated carbon. In this study, biomass carbon (AC) was prepared from corn stover as raw material. Preparation of nitrogen-containing biomass carbon (AC-N) using melamine as nitrogen source. Preparation of iron-loaded biomass carbon (AC-Fe) and iron-nitrogen-loaded iron biomass carbon (AC-N-Fe) using AC and AC-N as carriers and ferric nitrate as iron source. Choosing the different concentrations, temperatures, adsorption times to explore the adsorption properties of different carbons on copper ions. The results show that the adsorption performance of modified biomass carbon on copper is much greater than that of the original carbon (AC), and the modification is effective.

1. Introduction

Copper is widely used in chemical, steel and other industries. With the development of urbanization and industrialization in China, industrial pollution and urban pollution are becoming more and more serious. The discharge of a large amount of industrial wastewater makes more and more copper ions in the environment, and the damage to the ecological environment is also increasing. In China's "Sanitary Standard for Drinking Water (GB 5749-2006)", the limit of medium copper in drinking water is 1.0 mg / L. Therefore, it is quite necessary to properly handle copper in the environment.

Corn is the main crop in China. A small part of the straw produced each year is used as feed, most of which is incinerated or landfilled, lacking straw treatment mechanism. Creating a variety of ways to deal with straw has become a hot spot. Using waste corn stover as biomass carbon can not only recycle field straw resources, but also reduce the phenomenon of burning straw. The use of biomass carbon as an adsorbent material to adsorb copper ions in wastewater has the advantages of simple operation, wide source and low cost.

Shi Rui used corn stalk as the raw material of activated carbon, catalyzed by using zinc chloride to prepare activated carbon, and adsorbed the waste of methylene blue dye to study its adsorption behavior. Experiments show that this kind of activated carbon has good adsorption capacity for methylene blue wastewater and can be applied to wastewater treatment[1]. Xu Zhihua of Shanghai University of Science and Technology, etc., activated carbon as a carrier, modified by adding $\text{Fe}_2(\text{SO}_4)_3$ solid, and prepared nano-iron/activated carbon material by precipitation method. The experiment shows that when the pH is 6, the amount of copper ions adsorbed by the material can reach 18.73 mg/g, which is 1.5 times higher



than that of ordinary activated carbon[2]. Liu Yunpeng of Zhejiang University, on the basis of previous studies on nitrogen-containing mesoporous carbon, pointed out the shortcomings of the current preparation of nitrogen-containing ordered mesoporous carbon, and also prospected its development[3].

Karen C. Bedin in the hydrothermal treatment of sugarcane, chemically activated by KOH to obtain spherical carbon, its specific surface area is $1534\text{m}^2/\text{g}$, the maximum adsorption capacity of single layer is $704.2\text{mg}/\text{g}$, the highest in all document records found[4]. Mahaninia et al. used two different methods to aminate carbon materials and studied the adsorption behavior of copper ions[5]. Yantasee used nitric acid to nitrate activated carbon, added sodium bisulfite in the alkaline environment of ammonia to reduce the nitro group to amino group, and formed aminated activated carbon to adsorb copper ions in water. [6]. Ates studied the yield and composition of sesame straw under rapid pyrolysis solution by temperature, straw diameter and nitrogen flow rate[7].

2. Research content

In this experiment, the waste corn stover was used as the biomass carbon preparation material, and the biomass carbon was prepared and modified, and the adsorption capacity was determined by the copper ions adsorption experiment. Choosing the different concentrations, temperatures, adsorption times to explore the adsorption properties of different carbons on copper ions.

2.1. Preparation of biomass mesoporous carbon

2.1.1. Preparation of biomass liquefaction. The corn stover core was pulverized through a 50 mesh sieve and placed in a drying oven at 105°C for more than 24 hours. Corn stalk core powder 4 g, phenol 20 g, and 36% sulfuric acid were sequentially added to a 500 ml three-necked flask. The flask was placed in an oil bath at 170°C and stirred for 2h. After the liquefaction time is over, the vacuum pump is used for suction filtration, and the liquefied material is diluted with a large amount of acetone, and then dried in an oven for more than 12 hours to obtain a biomass liquefied material.

2.1.2. Preparation of mesoporous carbon mesophase. Add 10g of liquefied solution to 90 ml of formalin solution, 3g of sodium hydroxide, 10g of F127, and place in a magnetic stirrer at 40°C for 20h. Then add hydrochloric acid to adjust the pH to 0.5, add 10.4 g of TEOS, continue the reaction for 8h. The sample was transferred to a flat bottom evaporating dish and placed in an oven at 100°C for 24h to obtain a flexible film which was a corn stalk-based carbon mesophase.

2.1.3. Preparation of mesoporous biomass carbon and its functional modification. The carbon mesophase was placed in a muffle furnace, heated to 700°C , carbonized for 2h, and the temperature increase rate was strictly controlled at $1^\circ\text{C}/\text{min}$. When the temperature was lowered to room temperature, AC was taken out. AC-N can be prepared by adding melamine to AC and repeating the above steps. AC and AC-N were washed in 4mol/L NaOH solution for 24h and then vacuum dried. Then, they were placed under mechanical stirring, and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in the suspension solution. The sample was taken out and fired in a tube furnace at 300°C for 4 h. The powder was placed in a nitrogen atmosphere tube furnace, the air flow rate was 200 ml/min, and the temperature was 800°C for 4h to obtain AC-Fe and AC-N-Fe.

2.2. Adsorption experiment

2.2.1. Isothermal adsorption experiment. The Cu^{2+} adsorption experiments on 4 carbons at 25°C are as follows: Preparing a $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution having a pH of 6, and the Cu^{2+} concentration gradient of 6,30,40,60,80,100,150,200mg/L, respectively. According to the concentration gradient, 25mL of different concentrations of CuSO_4 solution were taken, and 0.05g of carbon material was weighed and placed in a 100mL erlenmeyer flask for 2h. The concentration of copper ions in the filtrate was determined by atomic analyzer. Calculate the equilibrium adsorption amount of Cu^{2+} of different carbon

materials. The above experiment was repeated at 35°C and 45°C by selecting the biomass carbon material with the best adsorption effect on Cu²⁺.

The equilibrium adsorption amount (Q_e) calculation formula is

$$Q_e = \frac{V(C_0 - C_e)}{m}$$

In the formula, V is the volume (L) of CuSO₄ solution added in the experiment, C₀ and C_e are the concentration before adsorption and after adsorption for CuSO₄ solution(mg/L), respectively, m is the mass of biomass carbon material (g).

2.2.2. Kinetic experiment. Select 40mg/L in the isothermal gradient as the experimental concentration, and measure 500mL of the prepared CuSO₄ solution with a pH of 5 in a 500 mL beaker and place it in a magnetic stirrer to heat to 20°C. 0.1g of biomass carbon material was completely poured into the CuSO₄ solution and started to be timed, and 5mL of the solution was taken at 5s,15s,1min, 3min,5min,10min,15min,30min,45min,60min,75min,90min,105min and 120min,respectively. After filtration through a filter, the remaining Cu²⁺ concentration was measured using an atomic analyzer. The temperature during the experiment was changed, and two further kinetic experiments were carried out at 40°C and 60°C as described above.

3. Research result

3.1. Influence of material structure on adsorption performance

The Figure 1 shows the adsorption curves of AC-Fe, AC-N, AC-N-Fe, AC under static conditions at 25°C. It can be seen that as the concentration of the solution increases, the adsorption amount of AC-Fe, AC-N, AC-N-Fe to Cu²⁺ increases. The adsorption amount of Cu²⁺ is increasing rapidly, and the adsorption amount tends to be stable when the concentration of the solution increases to a certain extent. This is because the adsorption site on the carbon surface is saturated and the adsorption reaches equilibrium. The curve of AC-N is at the highest position, and the equilibrium adsorption amount is 11.339 mg/g. The equilibrium adsorption capacity of AC can only reach 5.441mg/g, which is 2.08 times different.

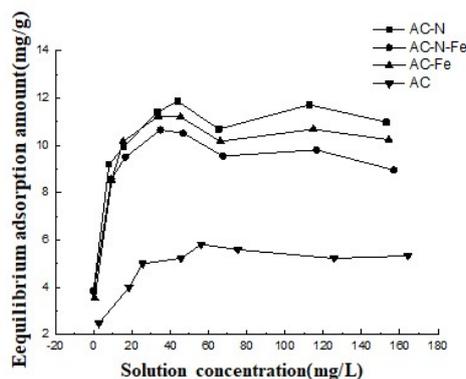


Figure 1. Isothermal adsorption curves of 4 carbon samples.

The adsorption capacity of biomass carbon is closely related to its specific surface area and pore structure, and also related to surface functional groups[8].It can be seen that after the addition of N element in AC, the original surface properties are changed, and the adsorption amount of AC-N is greatly increased compared with AC, indicating that the addition of N element increases the chemical adsorption performance of biomass carbon[9]. When Fe is introduced into biomass carbon, it also has a good catalytic effect on adsorption, and this state can promote the adsorption process[10].

3.2. Influence of temperature on adsorption performance

Figure 2 shows the static adsorption curve of AC-N on Cu^{2+} at three different temperatures of 25°C, 35°C and 45°C. It can be seen that the adsorption performance of AC-N on Cu^{2+} varies with the change of its temperature. When the concentration of Cu^{2+} in the solution is under 10 mg/L, the effect of temperature on the adsorption of Cu^{2+} is not obvious. When the concentration of Cu^{2+} in the solution continues to increase, the effect of temperature on adsorption is more obvious, and the adsorption capacity increases with the increase of temperature, and finally reaches the adsorption equilibrium. At the initial concentration of the solution was 200mg/L, the equilibrium concentrations were 153mg/L, 152mg/L, and 150mg/L at three temperatures, and the equilibrium adsorption amounts were 10.99mg/g, 11.60mg/g, and 12.63mg/g. This result indicates that the adsorption of Cu^{2+} by AC-N is an endothermic reaction, and the increase of temperature is favorable for adsorption[11].

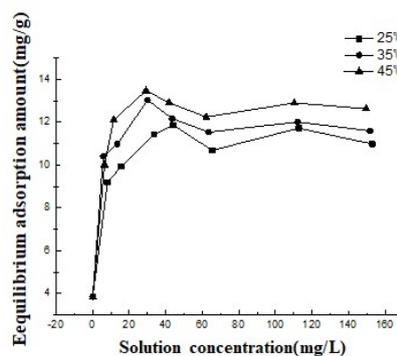


Figure 2. AC-N adsorption curve at 3 temperatures.

In order to further study the adsorption characteristics of AC-N on copper ions in solution, Langmuir, Freundlich, Redlich-Peterson and Temkin nonlinear isothermal models were fitted to the experimental data. The model equations and fitting results are shown in the Table 1. The Langmuir isotherm adsorption model is suitable for surface monolayer adsorption[12], the Temkin model is the diffusion interface model, and the Freundlich adsorption model is the empirical equation for surface energy isomerism. $n > 1$ is preferential adsorption and $2 < n < 10$ is favorable adsorption[13]. As can be seen in Table 1, the correlation coefficient R^2 of the Temkin model is the highest compared with the other three models, indicating that the model is more suitable for describing the adsorption behavior of AC-N on copper ions. In the Freundlich model, the values of n are all greater than 1, indicating that adsorption is relatively easy to occur, and the adsorption of copper ions by AC-N is preferential adsorption[14].

Table 1. Isothermal adsorption model fitting results.

model	Model equation	Parameters	25°C	35°C	45°C
Langmuir	$q_e = kq_m c_e / (1 + kc_e)$	q_m (mg/g)	0.51106	1.2472	11.55015
		k (L/mg)	11.60845	12.11577	12.38962
		R^2	0.61715	0.66622	0.8862
Freundlich	$q_e = K_F c_e^{1/n}$	K_F (L/mg)	7.30092	8.32693	8.0501
		n	9.76165	11.28679	8.95214
		R^2	0.88769	0.83114	0.8048
Redlich-Peterson	$q_e = K_R c_e (1 + \alpha c_e^\beta)$	K_R (L/mg)	1.2049E-4	8.8867E-5	1.08E-4
		α (L/mg)	60643	93790	74630
		β	-0.89801	-0.91184	-0.8883
		R^2	0.86418	0.79639	0.76477
Temkin	$y = b \ln A_r + b \ln x$	A_r (L/mg)	9488	46684	1282
		b (L/mg)	0.83956	0.80847	1.13812
		R^2	0.93248	0.90215	0.89289

3.3. Influence of temperature on adsorption performance

In this experiment, the set temperature was 20,40,60°C, the concentration was 40mg/L, and a quantitative solution was taken at a set time to measure the concentration of copper ions. The kinetic experiments aimed to study the effect of AC-N on the adsorption behavior of copper ions in solution by time, and used the quasi-first-order equation, quasi-second-order equation and Elovich equation to fit the adsorption data of copper ions on AC-N. The fitting result is shown in Table 2, and the fitting formula is as follows:

$$(1) \ln(1 - F) = -k_1 t$$

$$(2) \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

$$(3) q_t = (1/\beta^E) \ln(\alpha_E \beta_E) + (1/\beta_E) \ln t$$

Equations (1) and (2) and (3) are the equations of the quasi-first-order adsorption model, the quasi-secondary adsorption model, and the Elovich adsorption model, respectively. Where $F=q_t/q_e$, q_t and q_e are the Cu^{2+} adsorption amount of carbon material at time t and the equilibrium adsorption capacity of Cu^{2+} , k_1 is the first-order adsorption rate constant(/min); t/q_t is linear with t . k_2 is the quasi-second-order kinetic rate constant [g/(mmol·min)]; α_E is the initial adsorption rate constant in mg/(g·min), and β_E is the desorption rate constant in g/mg[1].

Looking at Table 2, as the temperature increases, the adsorption rate (k_1) increases slowly, indicating that the temperature rise is favorable for adsorption. The correlation coefficient R^2 of the quasi-first-order kinetic model fitting is relatively small, indicating that this kinetic model does not describe the experimental data well. The correlation coefficient R^2 of the quasi-second-order adsorption model is very close to 1, almost all points fall on the fitted curve, and the fitted adsorption amount is very close to the actually measured adsorption amount. The kinetic model can better fit the measured adsorption behavior of activated carbon on copper ions. This indicates that the copper ions in the solution diffuse from the outer surface of the activated carbon into the inner surface, and the adsorption of copper ions is mainly chemical adsorption [15]. The Elovich model has a poor effect on the adsorption fit, and the correlation coefficient R^2 does not exceed 0.8. Thus, the Elovich equation does not apply to the fitting of AC-N to the adsorption behavior of copper ions

Table 2. Kinetic model fitting results.

Kinetic model	Model equation	Parameters	20°C	40°C	60°C
Quasi-first-order equation	$\ln(1 - F) = -k_1 t$ $F = q_t/q_e$	$k_1(\text{min})$	0.02789	0.0278	0.02825
		$q_e(\text{mg/g})$	13	14	15
		R^2	0.71614	0.53022	0.52605
Quasi-second-order equation	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	$k_2[\text{g}/(\text{mg}, \text{min})]$	0.1053	0.1819	0.2579
		$q_0(\text{mg/g})$	12.84	13.85	16.31
		R^2	0.999	0.998	0.999
Elovich equation	$q_t = (1/\beta^E) \ln(\alpha_E \beta_E) + (1/\beta_E) \ln t$	$\alpha_E[\text{mg}/(\text{g}, \text{min})]$	35111	4299	77300
		$\beta_E(\text{g/mg})$	1.14248	0.8691	0.00168
		R^2	0.75564	0.77331	0.66755

4. Conclusion

In this paper, corn stalk is used as raw material, liquefaction technology used in the preparation of AC, melamine is used as nitrogen source, ferric nitrate is used as iron source, and AC-Fe, AC-N and AC-N-Fe are obtained by modification of AC. Through the adsorption experiments of Cu^{2+} , it is proved that the modification of biomass carbon improves its adsorption capacity and the modification is effective. This provides a viable method for the treatment of industrial wastewater. The addition of N element to the biomass carbon can improve the stability of the carbon material, enrich the pore structure. The addition of Fe element increases the specific surface area of the biomass carbon and is also advantageous for adsorption.

From the isothermal adsorption data, AC-N has the best adsorption effect on copper ions in solution, and the maximum adsorption capacity is 11.339mg/g at 25°C. The adsorption performance of AC-N-Fe is not as good as that of AC-N, indicating that proper modification can obtain activated carbon with excellent performance. The Temkin isotherm model is more suitable than other models to describe the adsorption behavior of AC-N on copper ions.

From the kinetics fitting situation, the quasi-second-order kinetic model can better fit the measured adsorption behavior of activated carbon on copper ions. The adsorption of copper ions by AC-N is mainly chemical adsorption[16].

References

- [1] Shi Rui, Li Yili, Yin Jing, Yang Shanshan. Preparation of activated carbon from corn straw and research of adsorption kinetics [J]. Chinese Journal of Environmental Engineering, 2014, 08: 3428-3432.(in chinese)
- [2] Xu Zhihua, Zhang Daofang, Chen Weifang. Preparation of nano-iron/activated carbon new materials and their adsorption properties for copper ions[J]. Journal of Water Resources and Water Engineering, 2015, 02: 7-11. (in chinese)
- [3] Liu Yunpeng, Zhou Jie, Li Zhongjian, Lei Lecheng. Research progress of nitrogen-doped ordered mesoporous carbon [J]. Modernization, 2014, 06:19-22+24. (in chinese)
- [4] Bedin, KC; et al. KOH-activated carbon prepared from sucrose spherical carbon: Adsorption equilibrium, kinetic and thermodynamic studies for Methylene Blue removal[J]. Chemical Engineering Journal. 286, 476-484, Feb. 15, 2016.
- [5] Mahaninia M H,Rahimian P,Kaghazchi T.Chinese J.Chem.Eng.,2015,23(1):50.
- [6] Yantasee W,Lin Y,Fryxell G E,Alford K L,Busche B J,Johnson C D.Ind. Eng. Chem. Res. ,2004,43(11):2759.
- [7] Ates F, Putun E, Putun A E. Fastpyrolysis of sesame stalk: yields and structural analysis of bio-oil[J]. Journal of Analytical and Applied Pyrolysis, 2004 (71):779-790.
- [8] Li Lili. Study on the adsorption and desorption properties of modified activated carbon fiber and starch charcoal[D].China University of Petroleum,2008. (in chinese)
- [9] OKAMURA J, NISHIYAMA S, TSURUYA S H, et al. Formation of Cu -supported mesoporous silicates and aluminosilicates and liquid -phase oxidation of benzene catalyzed by the Cu -mesoporous silicates and aluminosilicates [J]. JMolCatal. A, 1998, 135: 133 -142.
- [10] Gao Wenjun. Study on Graphitization and Magnetic Functionalization of Mesoporous Carbon by Iron Catalyst[D].Shanghai Normal University,2011. (in chinese)
- [11] Guo Zhuo, Zhang Weiwei, Wang Lifeng, Gao Zhan. Preparation of Novel Mesoporous Carbon and Adsorption Kinetics of Rhodamine B[J]. Modern Chemical Industry, 2006, S2: 95-98.
- [12] Sánchez-Sánchez A, Suárez-García F, Martínez-Alonso A, et al. Aromatic polyamides as new precursors of nitrogen and oxygen-doped ordered mesoporous carbons [J].Carbon. 2014,70: 119-129.
- [13] Wang Yu. Adsorption of Heavy Metal Ions in Water by Modified Activated Carbon[D]. Suzhou University of Science and Technology, 2015. (in chinese)
- [14] Liu R L, Shi Y F, Wan Y, et al. Triconstituent Co-assembly to Ordered Mesoporous Polymer-Silica and Carbon-Silica Nanocomposites and Large-Pore Mesoporous Carbons with High Surface Areas. Journal of the American Chemical Society, 2006, 128(35):11652-11662.
- [15] Geng Lili. Study on Preparation of Activated Carbon by Phosphoric Acid Activated Cotton Stalk[J]. Anhui Agricultural Sciences, 2014, v.42; No.45926:9111-9113. (in chinese)
- [16] Lu A, Kiefer A, Schmidt W, et al. Synthesis of polyacrylonitrile based ordered mesoporous carbon with tunable pore structures[J].Chemistry of Materials.2003,16 (1) :100-103.