

# Synthesis of Poly(acrylic acid)-Grafted Carboxymethyl Cellulose for Efficient Removal of Copper Ions

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**Abstract:** Biocompatible and high content grafted carboxymethyl cellulose-g-poly(acrylic acid) powder was successfully synthesized in an aqueous system, and used as adsorbents for the removal of Cu(II) in aqueous solution. The copolymer was characterized by FT-IR and SEM techniques. Graft copolymerization introduced a large number of carboxyl groups in the polymer and caused the micro-surface of the material to be porous. The fundamental adsorption behaviors of the material were studied. The adsorption kinetics was well fitted with pseudo-second order equation, while the adsorption isotherm preferred to be described the Langmuir equation. The maximum adsorption capacity obtained from the Langmuir model was 154.32 mg/g, indicating that the adsorption capacity of carboxymethyl cellulose was improved remarkably after grafting poly(acrylic acid). Moreover, Fourier transform infrared spectroscopy (FT-IR) has been used to investigate the adsorption mechanisms at molecular levels, which revealed that carboxyl groups are facile to form bidentate carboxylates with metal ions. Thus, this environment friendly copolymer will be a promising candidate for application in removal of heavy metal ions.

**Keywords:** Carboxymethyl cellulose-g-acrylic acid; grafting copolymerization; adsorption; copper ions

## 1 Introduction

Over the years, with rapid development of modern industries, heavy metal commination in water resources has increasingly become an urgent issue, of great concern to both the ecological system and public health. Several metals are considered to be toxic, such as nickel, zinc, copper, mercury, cadmium and lead. Among these metal pollutions, copper may cause temporary stomach and intestinal disorders, kidney or liver damage, and even cancer in human beings as a result of its cumulative effect [1]. The copper-containing materials are widely used in various industrial sectors though they are still hard to separate from wastewater [2]. Several treatment technologies are available to reduce the heavy metal concentrations in water and wastewater, including coagulation/coprecipitation, ion exchange, electrochemical method, adsorption, membrane separation and solvent extraction [3,4]. Among these methods, adsorption has gained wide attention and has been continuously developed because of its cost effectiveness, simplicity of operation, high efficiency, easy recovery and sludge-free operation.

Recently, the search for eco-friendly materials as the adsorbent with low cost, and with no hazardous by-products generation has been in focus [5-10]. In this perspective, cellulose and its derivatives are considered as outstanding candidates due to their environmental-friendly characteristics, low cost, less sludge generation and wide source [5]. Carboxymethyl cellulose (CMC) is an attractive and promising derivative of cellulose in adsorbent fields because of its strong adsorption to a wide range of heavy metals. Baiya et al. prepared the CMC/PVA/GA hydrogel for selective adsorption of Cu(II) ions [11]. Godiya et

al. have fabricated a CMC/PAM compound with superior adsorption capacity for efficient removal of heavy metal ions from the wastewater. They found that copper-loaded products can be used as catalysts after in situ reduction of adsorbed Cu(II) [12]. The CMC and graphene were combined to form a porous structure, which enhanced the ability to adsorb heavy metal ions [13]. To date, the improved performance for the adsorption of heavy metal ions by CMC-based materials is still a challenge although researchers have made great efforts.

A large number of chemical and physical modifications devote to the application of carboxymethyl cellulose materials using crosslinking, grafting of functional side chains and blending polymer or inorganics for the removal of metals from wastewater has grown rapidly [14-18]. Owing to great chelating effects of carboxyl groups, poly(acrylic acid) (PAA) has attracted increasing attention as modifier material, which contains a carboxyl group in each repeated unit, and favor adsorption of metal ions [14]. Most efforts have been made to blending or in situ grafting PAA on carboxymethyl cellulose for enhance metal ions adsorption capacity [15,16]. But the copolymers obtained in these ways often contain ultra-short chains and low levels of PAA. Moreover, some of these preparation methods use organic solvents, causing secondary pollution [15]. Therefore, a higher grafting content should be obtained to enhance adsorption capacity, which can be accomplished from copolymerization of CMC containing double bonds with acrylic acid in the water. Furthermore, such copolymers are biodegradable and thus can reduce secondary wastes.

In this article, the carboxymethyl cellulose-g-poly(acrylic acid) (CMC-g-PAA) is synthesized via graft copolymerization of methacrylated carboxymethyl cellulose with acrylic acid in a homogeneous system, and the copolymer is characterized by FT-IR and SEM techniques. The adsorption capacity of the material for copper ions has been improved obviously after introducing carboxyl groups of long-chain PAA into the carboxymethyl cellulose. Various effecting parameters on the removal of Cu(II) from aqueous solution are investigated to determine adsorption behavior and performance of CMC-g-PAA, including contact time, initial concentration and pH value. Furthermore, the isothermal adsorption equilibrium and kinetics are also studied. The possible adsorption mechanism is further identified based on Fourier transform infrared spectroscopy.

## 2 Materials and Method

### 2.1 Materials

Sodium carboxymethyl cellulose (Mw 90 KDa, substitution degree = 0.7) was purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China) and used without further purification. Acrylic acid (AA), Methacrylic anhydride and Potassium persulfate ( $K_2S_2O_8$ ) were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).  $K_2S_2O_8$  was recrystallized from distilled water. All other reagents were of analytical grade and used without further purification. Distilled water was used in all experiments.

### 2.2 Preparation of Carboxymethyl Cellulose-g-poly(acrylic acid) (CMC-g-PAA)

The CMC-g-PAA powder was prepared by two steps and the details were as follows. Briefly, 4 g of carboxymethyl cellulose was dissolved in 150 mL of water in a 250 mL round-bottom flask equipped with a magnetic stirring. 7 mL of methacrylic anhydride was added and then the pH of the mixture was adjusted to around 8 with a 2 M NaOH solution. After stirring for 24 h at 0°C, the mixture was precipitated and washed with ethanol to remove the remaining methacrylic acid and methacrylic anhydride. The product was collected by filtration and dried to afford methacrylated carboxymethyl cellulose (MCC) as a white powder.

Methacrylated carboxymethyl cellulose (4 g) was dissolved in 100 mL distilled water with stirring and then 8 g of neutralized acrylic acid was added to the solution. 10 mL aqueous solution with 0.2 g potassium persulfate was subsequently added to the system. Polymerization was carried out at 75°C and proceeded for 4 h under nitrogen atmosphere. The product was obtained in ethanol and made free from homopolymer by exhaustive extraction with hot deionized water and ethanol for 24 h. Finally, the

powdered product was dried in vacuum at 60°C up to constant weight, and stored for further experiments. Additionally, the graft content (G) was calculated as follows:

$$G = \frac{W_g - W_0}{W_0} \times 100\% \quad (1)$$

where  $W_g$ ,  $W_0$  are weights of copolymer and MCC, respectively.

### 2.3 Characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 510p spectrometer. The samples were mixed with KBr and pressed to a thin plate for measurement. Scanning electron microscopy (SEM) studies were carried out in an S-4800 SEM instrument (Hitachi) after coating the sample with gold film. Thermogravimetry (TG) curves were obtained on a Henven HTG-3 thermometer at a heating rate of 15°C min<sup>-1</sup> from 5°C to 750°C. The Zeta potential of the sample was obtained with Zetaplus (Brookhaven Instruments Corp.). All results were the average of triplicate measurements. Copper ions content in the solution was determined using the oxalic acid bis-cyclohexylidene hydrazide spectrophotometry at the wavelength of 600 nm.

### 2.4 Adsorption Experiment

Adsorption experiments were conducted by varying initial copper ions concentration, contact time, temperature and pH value under the aspects of adsorption isotherms and adsorption kinetics. Typical experiment was performed under 200 rpm with stirring for 3 h, which was carried out in a series of 100 mL round-bottom flasks containing 50 mg of adsorbent powder and 25 mL of Cu<sup>2+</sup> solution. After adsorption, the adsorbents were separated by direct filtration and the final Cu<sup>2+</sup> concentrations in the solution were determined. The amount of metal ions adsorbed onto adsorbent was calculated according to the following equation:

$$q = \frac{(C_0 - C)V}{m} \quad (2)$$

where  $q$  is the amount of sorbate per adsorbent (mg/g);  $C_0$  and  $C$  are the liquid phase concentrations of Cu(II) at initial and final time, respectively (mg/L);  $V$  is the volume of the solution (L);  $m$  is the mass of dry adsorbent (g).

The effect of initial pH on adsorption behavior of CMC-g-PAA for Cu(II) was studied by varying pH value from 3.0 to 7.0 at 30°C for 3 h. The initial concentration of Cu(II) was 400 mg/L, and pH value was adjusted by adding appropriate concentrations of HCl or NaOH solutions. For the adsorption kinetic studies, 400 mg/L of Cu(II) solutions were contacted with 50 mg of adsorbent with different contact time (10 min to 8 h) at 30°C.

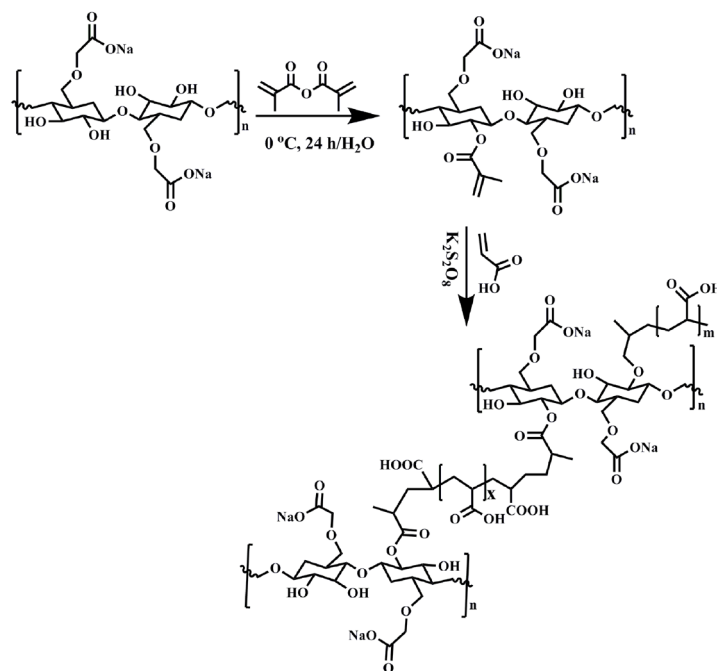
Equilibrium isotherms were used to determine the adsorbent capacity for metallic ions. Herein, Langmuir and Freundlich models were selected to demonstrate the adsorption equilibrium between the adsorbent and metal ions. Adsorption isotherm was instigated by varying the initial Cu(II) concentration from 25 mg/L to 600 mg/L for 3 h. The experiments were carried at pH = 6 and 20°C, 30°C, 40°C, respectively.

## 3 Results and Discussion

### 3.1 Characterization of CMC-g-PAA

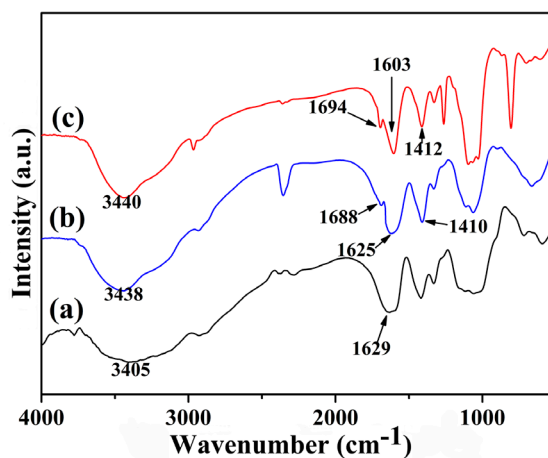
The procedure to prepare CMC-g-PAA power consists of two steps, as shown in Scheme 1. The methacrylated carboxymethyl cellulose was prepared by reacting carboxymethyl cellulose with methacrylic anhydride. Subsequently, the cross-linked carboxymethyl cellulose-g-poly(acrylic acid) (CMC-g-PAA) was synthesized by copolymerization of methacrylated carboxymethyl cellulose with acrylic acid in the presence of potassium persulfate. According to previous reports, the degree of methacrylation modification on carboxymethyl cellulose was over 11% [19]. From the calculation, the graft content of CMC-g-PAA was beyond 88%, and more obvious than that for most similar cellulose-

based copolymers reported by others [20,21].



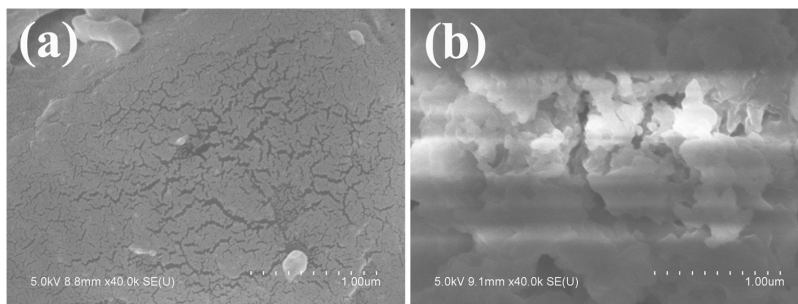
**Scheme 1:** Schematic representation for the synthesis of CMC-g-PAA

Fourier transform infrared (FT-IR) spectra were used to identify the groups involved in the reaction, and spectra of carboxymethyl cellulose, and CMC-g-PAA were shown in Fig. 1. For carboxymethyl cellulose, a broad band at around 3405 cm<sup>-1</sup> was corresponding to hydroxyl groups stretching vibration of cellulose. The peak at 1629 cm<sup>-1</sup> was attributed to the asymmetric stretching vibrations of carboxylate groups stemming from CMC. The FT-IR spectrum of the CMC-g-PAA was shown in Fig. 1(b). Comparing with the spectrum of carboxymethyl cellulose, the broad adsorption band at 3405 cm<sup>-1</sup> (hydroxyl groups) was shifted to high wave number and became sharp, while the new peak at 1688 cm<sup>-1</sup>, which can be assigned to stretching C=O vibration stemming from poly(acrylic acid), appeared. The results indicated that the poly(acrylic acid) chains were grafted on carboxymethyl cellulose through polymerization to form graft copolymer.



**Figure 1:** FT-IR spectra of carboxymethyl cellulose (a), CMC-g-PAA before (b) and after adsorption of Cu(II) (c)

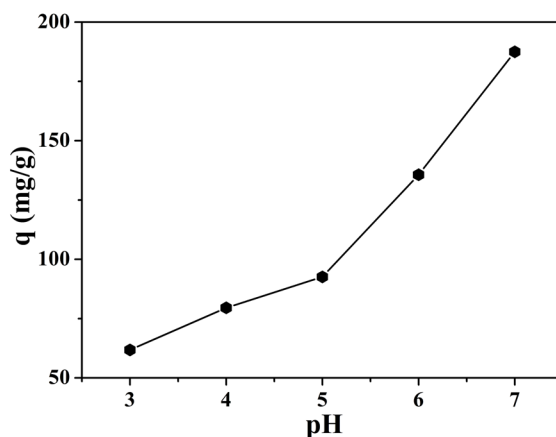
Fig. 2 shows the scanning electron microscopy (SEM) photographs of carboxymethyl cellulose and CMC-g-PAA. It was clearly observed that cellulose presented an almost smooth and nonporous surface. In contrast, the surface of CMC-g-PAA was obviously rough and porous, providing great surface area for practically useful adsorption purposes.



**Figure 2:** SEM photographs of carboxymethyl cellulose (a: 40000 $\times$ ) and CMC-g-PAA (b: 40000 $\times$ )

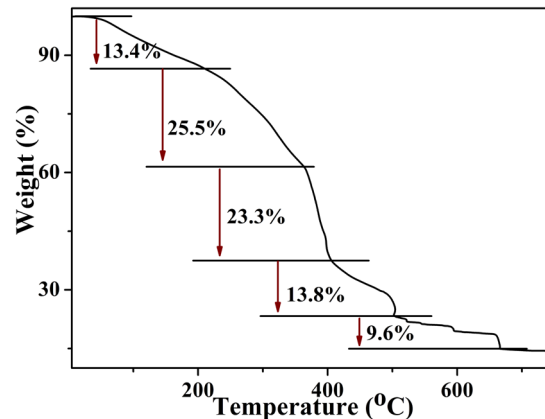
### 3.2 Adsorption Properties

Cu(II) has been employed as the model ion to demonstrate the adsorption properties of CMC-g-PAA. The pH of solution was known as one of the most important variables affecting the adsorption amount of heavy metal ions. Consequently, the effect of initial solution pH on Cu(II) removal by CMC-g-PAA is shown in Fig. 3. It was observed that the adsorption of Cu(II) increased gradually with increasing at pH < 5.0, then increased abruptly at pH 5.0-7.0. At low pH, carboxylic groups in the polymer existed in the form of -COOH rather than -COO<sup>-</sup>, which could go against the possibility of electrostatic interaction. Therefore, non-ionic bonding mechanism (for example hydrogen bonding) among functional groups occurs at low pH, which was responsible for lower metal ion adsorption efficacy. With an increase in pH values, the adsorption efficacy increased since the deprotonating of functional groups was favored at higher pH values, by which electrostatic interaction between the polymer backbone and Cu(II) ions. The Zeta potential of CMC-g-PAA was found to decrease from -24.2 mV to -40.0 mV with an increase in pH from 3.0 to 7.0, further confirming the above results. Moreover, the precipitation constant of Cu(OH)<sub>2</sub> is  $5.6 \times 10^{-20}$ , corresponding to Cu(II) precipitation at pH = 7.4, which means that the precipitation might play an important role beyond 7.4 [22]. Based on these points, to avoid the formation of precipitation in the aqueous solution, the pH of 6.0 was selected as the initial pH value of Cu(II) solution for subsequent adsorption experiment. The maximum Cu(II) uptake was 135.6 mg/g at a pH 6.0. Compared with pure cellulose reported previously [11,13], the CMC-g-PAA copolymer exhibited higher adsorption capacity.



**Figure 3:** Effects of initial solution pH on the Cu(II) uptakes of CMC-g-PAA. The initial concentration of Cu(II) in each solution was 400 mg/L, T = 30°C

Thermal analyses curves were recorded in order to further confirm the adsorbing efficacy of adsorbent to Cu(II). As shown in Fig. 4, the polymer-Cu complex was degraded in five well-distinguished steps. The first step ranges between 25 and 210°C with 13.4% of the adsorbed and bound water weight loss. The second step was recorded in the temperature range of 211-365°C and related to the cellulose degradation [23,24]. The third step of weight loss starts at 366°C and that continues to 405°C, contributing to decomposition of the carboxyl groups of the PAA chain. The fourth step range of 406-502°C was associated with breakage of PAA chain [25]. The fifth step in the interval of 503-666°C was due to the decomposition and oxidation of the residual polymers. The final remnant weight of 14.4% attributed to copper oxide arisen from high temperature oxidation. It has been calculated that Cu(II) uptakes of CMC-g-PAA was 135.6 mg/g consistent with those mentioned above.

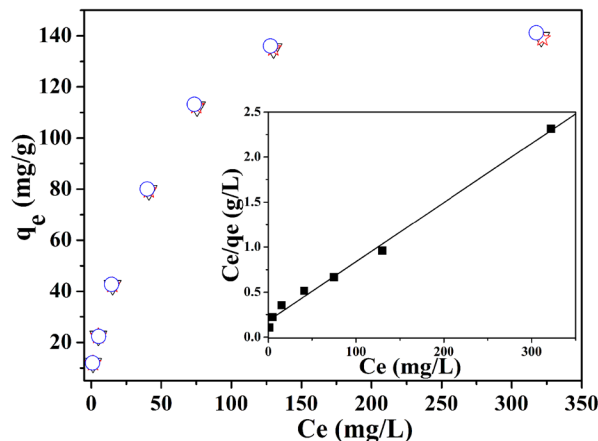


**Figure 4:** Thermogravimetric analysis TGA for adsorption of Cu(II) on CMC-g-PAA

It is well known that poly(acrylic acid) has poor biodegradability and thus limit their practical application. Thus, the strategy by grafting PAA on degradable carboxymethyl cellulose can not only enhance metal ions uptake but also improve biodegradability. Overall, CMC-g-PAA could be considered as a promising adsorption adsorbent for the removal of copper ions due to good biodegradability and adsorption capacity.

### 3.3 Adsorption Isotherms

The adsorption isotherm can indicate the interactive behaviors between the solutes and adsorbents and illuminate the properties and affinity of the adsorbent. The adsorption isotherm was measured at varied temperatures and pH = 6.0, which was presented in Fig. 5. It illuminated that the equilibrium amount of the adsorbed metal ions was almost not affected by temperature. In addition, it was found that the total amount of Cu(II) adsorbed increased sharply with the initial concentrations of metal ions increasing at the beginning, and then reached to surface saturation at high concentrations. This was attributed to an increase in Cu(II) concentration, which can enhance the permeation of metal ions into the polymer networks as a result of an increase in the driving force of concentration gradient. The correlation of equilibrium data was analyzed by the most commonly isotherm models, namely Langmuir and Freundlich model, and the adsorption mechanism was further investigated.



**Figure 5:** Adsorption isotherm of Cu(II) on CMC-g-PAA (pH = 6.0) at different temperatures: 20°C (▽), 30°C (☆), and 40°C (o). The inset shows the linear fitting results of the Langmuir model for Cu(II) adsorption on adsorbent at 30°C

Based on the assumption of a structurally homogeneous adsorbent, Langmuir isotherm was the commonly used model for monolayer adsorption process [26]. It can be represented as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \tag{3}$$

where  $q_e$  and  $C_e$  are the amount adsorbed (mg/g) and the adsorbate concentration on solution (mg/L), both at equilibrium;  $b$  is the Langmuir adsorption constant related to the energy of adsorption; and  $q_m$  is the maximum adsorption capacity of adsorbent (mg/g).

The Freundlich model was employed to describe heterogeneous system assumption of an exponentially decaying adsorption site energy distribution [27]. The equation can be expressed as:

$$\log q_e = \frac{1}{n} \log C_e + \log K_f \tag{4}$$

where  $K_f$  is the Freundlich isotherm constant, and  $1/n$  (dimensionless) is the heterogeneity factor.

**Table 1:** The isotherms parameters for Cu(II) adsorption onto CMC-g-PAA at various temperatures

Adsorbent	T (°C)	$q_{m,exp}$ (mg/g)	Langmuir model			Freundlich model		
			$q_{m,cal}$ (mg/g)	$b$	$R^2$	$K_f$	$n$	$R^2$
CMC-g-PAA	20	139.25	152.91	0.035	0.994	11.18	2.04	0.969
	30	139.02	152.2	0.036	0.993	11.24	2.05	0.968
	40	141.21	154.32	0.037	0.992	12.35	2.12	0.967

The experimental data was fitted based on the Langmuir and Freundlich models. The model parameters obtained are all listed in Tab. 1 and adsorption isotherms are shown in Fig. 5. Since there was no evident temperature dependence on adsorption capacity for CMC-g-PAA as mentioned above, the fitting result by Langmuir model at 30°C was selected and shown in the inset of Fig. 5. As seen from Tab. 1, the high correlation coefficients ( $R^2$ ) values for the Langmuir isotherm suggested that the Langmuir model fits fairly well with the experimental data points. The maximal Cu(II) uptakes calculated from Langmuir model were close to corresponding experimental data. It can be concluded that the monolayer Langmuir adsorption isotherm was suitable to explain the adsorption of Cu(II) onto CMC-g-PAA. In comparison to other reported cellulose-based materials as listed in Tab. 2, the CMC-g-PAA exhibited significantly higher capacity to adsorb Cu(II) ions. Although the adsorption capacity of pure poly(acrylic

acid) is higher than that of the copolymers, the poor biodegradability of pure poly(acrylic acid) limits its application in water purification.

**Table 2:** Comparison of maximum adsorption capacities of various adsorbents for Cu(II)

Adsorbents	Adsorption capacities(mg/g)	Reference
Cellulose hydrogels	28.4	[2]
Carboxymethyl cellulose/PVA hydrogels	2.3	[11]
Cellulose modified with TDI	47.61	[28]
Wheat straw cellulose-based hydrogels	130.0	[29]
HEC-EDTA	77.1	[30]
Sulfonated cellulose	17.4	[27]
CMC-g-PAA	141.21	This work
Poly(acrylic acid)	147.0	[31]

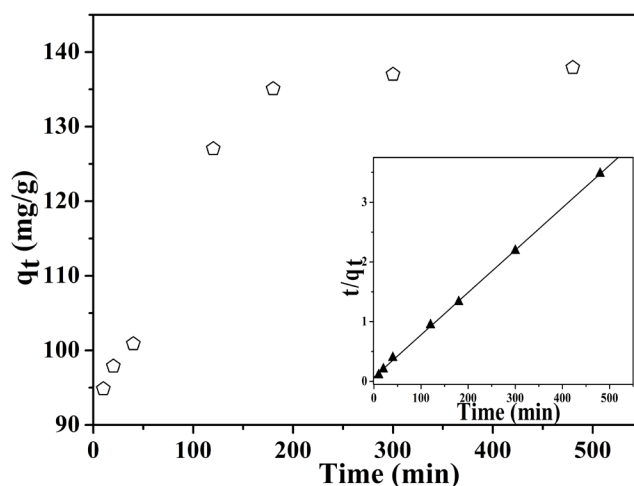
In order to determine the degree of suitability of adsorbent toward Cu(II) ions, a dimensionless constant ( $R_L$ ) called separation factor can be obtained by:

$$R_L = \frac{I}{I + bC_0} \quad (5)$$

where  $b$  is the Langmuir constant and  $C_0$  (mg/L) is the initial concentration of Cu(II) ions in solution. The value of  $R_L$  indicated the tendency of the isotherm to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ). Greater affinity between the adsorbent and the adsorbate was inferred when  $R_L$  was smaller. The constant  $b$  at various temperatures all showed positive values from Tab. 1. Thus, the values of  $R_L$  for CMC-g-PAA at every initial concentration of copper ions were all smaller than 1.0, signifying that a favorable adsorption of metal ions [32].

### 3.4 Adsorption Kinetics

To examine the controlling mechanism for the adsorption process, kinetic models have been used to assess the experimental data. The typical kinetic adsorption results of metal ions on adsorbent at 30°C were shown in Fig. 6. It can be seen that Cu(II) adsorption on CMC-g-PAA was a relatively fast process.



**Figure 6:** Effect of contact time on the adsorption of Cu(II) (pH = 6.0) at 30°C. The inset shows the linear fitting result of the pseudo-second order model for Cu(II) adsorption on adsorbent

In order to interpret the experimental data further, the pseudo-first order, pseudo-second order and intraparticle diffusion models have been applied to find out the adsorption mechanism [33]. The pseudo-



first order and pseudo-second order models were given as Eqs. (6) and (7), respectively:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where  $q_e$  and  $q_t$  (mg/g) are the amounts of Cu(II) ions adsorbed onto adsorbent at equilibrium and at time  $t$ , respectively.  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g/mg}\cdot\text{min}$ ) are the rate constant of pseudo-first and pseudo-second order adsorption, respectively.

The intraparticle diffusion equation was employed to verify whether the intraparticle diffusion behavior is the limiting step of the adsorption process [32]. It can be described as

$$q_t = k_p t^{0.5} + C \quad (8)$$

where  $q_t$  (mg/g) is adsorption capacity at time  $t$  (min),  $k_p$  ( $\text{mg/g}\cdot\text{min}^{1/2}$ ) is the intraparticle diffusion rate constant and  $C$  (mg/g) is related to the boundary layer thickness.

All of the experimental data have been linear fitted by the aforementioned kinetics models and the obtained parameters were all listed in Tab. 3. Based on the analysis of the correlation coefficients ( $R^2$ ), the pseudo-second order model was more appropriate to describe the adsorption kinetics behavior for Cu(II) onto the CMC-g-PAA powder. Moreover, the calculated  $q_e$  values also closed to the experimental data in the case of pseudo-second order kinetics. Therefore, the graphical presentation for pseudo-second order model was shown in the inset of Fig. 6. Theoretically simulated curve as solid lines fitted the experimental data quite well, showing that the rates of adsorption conformed to pseudo-second order kinetics, and the chemisorptions were the rate controlling mechanism. The results were consistent with those draws from adsorption isotherm analysis as mentioned above. Furthermore, the correlation coefficients of intraparticle diffusion model were quite low, revealing that the intraparticle diffusion was not rate-limiting step in the adsorption.

**Table 3:** Kinetic parameters for Cu(II) adsorption onto CMC-g-PAA at 30°C and pH = 6.0

Adsorbent	$q_{m, \text{exp}}$ (mg/g)	Pseudo-first order			Pseudo-second order			Intraparticle diffusion	
		$q_{e1\text{cal}}$ (mg/g)	$k_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_{e2\text{cal}}$ (mg/g)	$k_2 \times 10^{-4}$ (g/mg min)	$R^2$	$k_p$	$R^2$
CMC-g-PAA	138.01	50.78	0.0134	0.991	140.84	7.24	0.999	2.65	0.865

### 3.5 Adsorption Mechanism

For further investigation of the nature of adsorption and distinguish the possible adsorption sites of CMC-g-PAA, the FT-IR spectra for adsorbent before and after adsorption of Cu(II) ions were obtained and shown in Fig. 2. After adsorption, the asymmetric O-C-O vibration absorption of carboxyl group (COO-) has shifted from  $1625 \text{ cm}^{-1}$  to lower wave number of  $1603 \text{ cm}^{-1}$ , while the symmetric vibration absorption band of carboxyl group remains almost the same ( $1410\text{-}1412 \text{ cm}^{-1}$ ), implying that carboxyl groups were also involved in the adsorption process. In addition, the separation ( $\Delta$ ) between the symmetric and antisymmetric O-C-O stretching modes of the coordinated carboxylate anions in CMC-g-PAA was 191. According to previous study [34], the  $\Delta$  value for bidentate carboxylates was less than or equal to that from the free formate, for which the value of the sodium salt was  $241 \text{ cm}^{-1}$ . Therefore, the FT-IR results from polymer-Cu complex has proved the existence of bidentate carboxylates. It was obviously that the bidentate structures were beneficial to be adsorption of more Cu(II) ions for carboxyl group, which might be the reason that PAA grafted on celluloses had higher adsorption capacity.

#### 4 Conclusions

The cellulose based copolymer was designed and synthesized from carboxymethyl cellulose and acrylic acid, and characterized by FT-IR and SEM. The cellulose skeleton endowed the biodegradability for materials, meanwhile, the poly(acrylic acid) provided abundant carboxyl groups using as adsorption sites. Thus, the copolymer showed good affinity to  $\text{Cu}^{2+}$  ion, with the maximum adsorption capacity of 141.21 mg/g. Results from isotherms and kinetics study revealed that the adsorption isotherms obeyed the Langmuir equation and the adsorption kinetics were well described by the pseudo-second order equation. It indicated that the Cu(II) adsorption behavior of adsorbent was monolayer chemisorption. FT-IR illustrated that bidentate chelating interaction between the carboxylate groups and copper ions was the governing adsorption mechanism. The utilization of cellulose derived from plant fibers as the raw materials for the adsorbent preparation not only resolves the environment issues but also offers a way to prepare a promising low cost adsorbent for removal of heavy metals from wastewater.

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**Conflict of Interest:** The authors declare that they have no conflict of interest.

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