



ISSN: 2230-9926

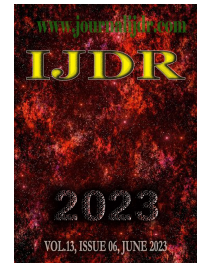
Available online at <http://www.journalijdr.com>

# IJDR

International Journal of Development Research

Vol. 13, Issue, 06, pp. 62903-62907, June, 2023

<https://doi.org/10.37118/ijdr.26794.06.2023>



RESEARCH ARTICLE

OPEN ACCESS

## EFFICIENTLY ADSORPTIVE REMOVAL OF CIPROFLOXACIN FROM WATER BY USING CROSS-LINKED CARBOXYMETHYL CELLULOSE

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### ARTICLE INFO

#### Article History:

Received 05<sup>th</sup> April, 2023

Received in revised form

29<sup>th</sup> April, 2023

Accepted 27<sup>th</sup> May, 2023

Published online 30<sup>th</sup> June, 2023

#### KeyWords:

Cross-Linking; Carboxymethyl Cellulose; Water; Ciprofloxacin; Adsorption.

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### ABSTRACT

A series of cross-linked carboxymethyl cellulose adsorbents (CCMCs) with different degrees of carboxymethyl substitution (the molar ratios of cellulose and chloroacetic acid were 1:0.7, 1:1, 1:1.2 and 1:1.5, respectively) were synthesized through etherification and crosslinking, and were used for the removal of a popular antibiotic, ciprofloxacin (CIP) from water. CCMCs presented high adsorption capacity for CIP owing to the electrostatic adsorption and hydrogen bonding interactions. With the increase of carboxymethyl substitution degree, the adsorption capacity of CCMCs for CIP gradually increased and the maximum theoretical adsorption capacity of CIP on CCMC 1.5 can reach to 2.821 mmol/g at pH 4.0. The adsorption isotherms obeyed the Langmuir model, which infer the adsorption process was monolayer adsorption. The adsorbent reached the adsorption equilibrium in approximately 60 min. The adsorption kinetics corresponded with the pseudo-second-order kinetic model, indicating that the adsorption was dominated by chemical adsorption. The adsorption capacity decreased with the increase of coexistence NaCl concentration, which further confirmed that the adsorption was dominated by electrostatic adsorption. This study demonstrated that CCMC, as an efficient adsorbent, has significant application potentials in removal of antibiotics from water.

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Citation: Yuyao Gong, Mengting Tan, Meng Lan, Li Na, Zhang Jun. 2023. "Efficiently adsorptive removal of ciprofloxacin from water by using cross-linked carboxymethyl cellulose". *International Journal of Development Research*, 13, (06), 62903-62907.

## INTRODUCTION

The abuse of antibiotics is widespread, and most antibiotics in the environment eventually enter the water environment [Khadra, 2019]. Ciprofloxacin (CIP), as a third-generation fluoroquinolone antibiotic, has been widely used in human clinical and livestock disease prevention due to the properties of broad spectrum, high efficiency and low toxicity [Kovtun, 2020]. Due to the stability and long half-life of heterocycles, it is not easy to degrade in water environment, and have been detected in soil, rivers, groundwater, sewage treatment plants and other environment [Wang, 2016; Ben, 2018]. It is of great significance to investigate the removal of CIP from water for preventing such drugs from entering the environment. To address the antibiotic pollution, many treatment technology, such as biological processes, sludge digestion, membrane filtration, advanced oxidation and adsorption has been used to remove antibiotics from water [Zhanguang Liu, 2013; Yifei Wang, 2015; Viviane Yargeau, 2008; Du, 2022].

However, adsorption method is a commonly used method owing to the properties of high efficiency, low cost and eased operation. Finding cheap, effective and reusable adsorbents is critical for adsorption technology [Igwegbe, 2021]. Cellulose is the most natural polymer in the world with the properties of biodegradability, chemical stability, thermal stability and low cost, which is a linear polymer linked by D-glucose-group with 1,4-β-glycoside bonds, riching in reactive -OH groups, and water solubility is greatly enhanced after appropriate modification [Gu, 2012]. Carboxymethyl cellulose (CMC), as one of the most common cellulose derivatives and few works were utilized for the removal of antibiotics [Yan, 2011; Hong, 2019]. Judging from the pKa value of CIP, a zwitterionic compound, contains amino and carboxyl groups [Carabineiro, 2012]. CMC can react with CIP through electrostatic interaction and hydrogen bonding. In this study, CCMCs with different degrees of substitution were designed and synthesized by etherification and cross-linking, and were used to adsorptive removal of CIP. Fourier transform infrared spectrum (FTIR), scanning electron microscope (SEM), the specific surface area and thermogravimetric analysis were utilized for characterization of CCMCs.

The fundamental CIP adsorption behavior of CCMCs, including the pH effect, adsorption equilibrium, adsorption kinetic and interference of coexisting inorganic salts, were investigated, respectively. The adsorption mechanisms were also discussed in detail.

## MATERIALS AND METHODS

**Chemicals:** Cellulose (analytical grade), chloroacetic acid (analytical grade), epichlorohydrin (analytical grade), CIP (>98%) were purchased from Aladdin. Hydrochloric acid (analytical grade), sodium hydroxide (analytical grade) and sodium chloride (analytical grade) were purchased from Tianjin Damao Chemical Reagent Factory.

**Preparation of CCMCs:** 5 g cellulose powder was dissolved in anhydrous ethanol, and NaOH solution was slowly added and stirred at 30°C, after alkalization for 1 h, a certain amount of chloroacetic acid was added, heated and stirred at 65°C for 3 h. CMC with different substitution degrees was obtained by adjusting the molar ratio of cellulose and chloroacetic acid, which were 1:0.7, 1:1, 1:1.2, 1:1.5, then they were sunk by ethanol, dried at 50°C and then ball ground into powder. 5 g CMC powder with different degrees of substitution was dissolved in 50 ml deionized water, and 0.1 mol/L NaOH solution was added for alkalization 1 h. 5 mL ECH was dropwise added, heat and stir at 60°C for 10 h, and sinked with ethanol, wash until neutral, dried and ball mill to obtain CCMCs powder (named CCMC 0.7, CCMC 1, CCMC 1.2, CCMC 1.5 according to different molar ratios). The preparation conditions and physical properties of CCMCs are shown in Table 2.1.

**Table 2.1 Preparation conditions and physical properties of CCMCs**

Adsorbent	Cellulose (g)	chloroacetic acid (g)	ECH (mL)	specific surface area (m <sup>2</sup> /g)
CCMC 0.7	5	2.041	5	0.381
CCMC 1	5	2.916	5	0.245
CCMC 1.2	5	3.499	5	1.005
CCMC 1.5	5	5.831	5	0.534

**Characterization of CCMCs:** CCMCs were measured by a Fourier transform infrared spectrometry (NEXUS870, NICOLET, USA) in wavenumber range of 500-4000 cm<sup>-1</sup>. CCMCs were observed by scanning electron microscopy (SEM, TM4000 Plus, Hitachi, Japan) under the accelerated voltage of 15.0 kV. The specific surface area of the adsorbents were determined by a surface area analyzer (ASAP2020, Micromeritics, USA). The thermogravimetric analysis of CCMCs was measured under air atmosphere with temperature range of 30 to 800°C and a heating rate of 20°C/min by a Thermogravimetric Analyzer (Pyris 1 DSC, PerkinElmer Corporation).

### Batch adsorption experiment

**pH effect:** 5 mg of CCMCs adsorbents with different carboxyl substitution degrees were added to 30 mL of CIP solutions with the initial concentration of 0.20 mmol/L at different pH values (pH 2.0-10.0), and then the mixtures were shaken in a thermostatic oscillator for 12 h at 180r/min under the temperature of 25°C to reach adsorption equilibrium. The CIP concentration was determined by ultraviolet spectrophotometer (U-2910, Hitachi, Japan). The adsorption capacity was calculated according to Equation (1): Where,  $C_0$  and  $C_e$  (mmol/L) are the initial and equilibrium concentrations, respectively.  $V$  is the volume of solution (mL);  $m$  (mg) is the mass of the adsorbent.

**Adsorption isotherms:** 5 mg CCMCs with different carboxyl substitution degrees were added into 30 mL CIP solutions with initial concentrations from 0.04 mmol/L to 0.28 mmol/L at initial pH 4.0, respectively. After continuous shaking at 25°C for 12 hours, the CIP concentration was measured after filtration, and the adsorption capacity was calculated by Equation (1).

The Langmuir and Freundlich models were utilized to fit the adsorption isotherms. The Langmuir model [14] can be written as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (2)$$

Where,  $q_e$  (mmol/g) is the adsorption capacity at adsorption equilibrium,  $C_e$  (mmol/L) is the concentration of CIP solution at adsorption equilibrium,  $q_m$  (mmol/g) is the theoretical saturated adsorption capacity, and  $b$  (L/mmol) is the Langmuir adsorption constant.

The Freundlich model [Freundlich, 1906] is expressed as follows:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f \quad (3)$$

Where,  $K_f$  is Freundlich isothermal constant and  $n$  is the heterogeneity factor, respectively.

**Adsorption kinetics:** 40 mg of CCMCs with different carboxyl substitution degrees were added to 240 mL CIP solutions respectively, with an initial concentration of 0.20mmol/L at pH 4.0 under continuous stirring at 25°C for 24 h. The CIP concentration were measured at different time intervals, and the adsorption capacity was calculated according to Equation (4).

$$q(t_i) = \frac{(C_0 - C_{t_i})V_0 - \sum_{j=1}^{i-1} C_{t_{j-1}} V}{m} \quad (4)$$

Where  $q(t_i)$ (mg/g) is the adsorption capacity of adsorbents at time  $t_i$ ;  $C_{t_i}$ (mg/L) is the concentration of CIP solution at  $t_i$ ;  $V_0$  (L) and  $V$  (L) are the total volume of the CIP and the sample volume taken out for CIP concentrations analysis, respectively;  $m$  (g) is the mass of the adsorbent.

The pseudo-first-order model [16] and pseudo-second-order model [Lagergren, 1989] were used to fit the experimental data. The pseudo-first-order model can be expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

Where,  $q_e$  (mmol/g) and  $q_t$  (mmol/g) represent the adsorption capacity after the adsorption equilibrium and at time  $t$  (min), respectively, and  $k_1$  (min<sup>-1</sup>) is the pseudo-first-order adsorption rate constant.

The formula of the pseudo-second-order model is written as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Where  $k_2$  (g·mg<sup>-1</sup>·min<sup>-1</sup>) is a pseudo-second-order adsorption rate constant.

**Influence of co-existing inorganic salt on adsorption:** 5 mg CCMCs were added to 30 mL CIP solution with an initial concentration of 0.20 mmol/L under the initial pH 4.0, and the coexisting NaCl concentrations were 0, 0.1, 0.5, 1, 5 and 10 mmol/L, respectively. After continuous shaking for 12 hours at 25°C, the CIP concentration was measured, and the CIP uptakes were calculated by Equation (1).

**Characterization of CCMCs:** The FTIR spectra of CCMCs with different carboxyl substitution degrees were shown in Fig. 1. The characteristic peak at 3342, 1589 and 1412  $\text{cm}^{-1}$  were related to the stretching of -OH group, and the asymmetric stretching and symmetric vibration of -COOH group, respectively, indicating the successful preparation of CCMCs [18]. From CCMC 0.7 to CCMC 1.5, the asymmetric expansion range of -COOH group became larger, demonstrating that the carboxyl substitution degree gradually increased. The strong peak near 1050  $\text{cm}^{-1}$  was ascribed to the bending vibration of C-O-C owing to the successfully cross-linked of CCMCs.

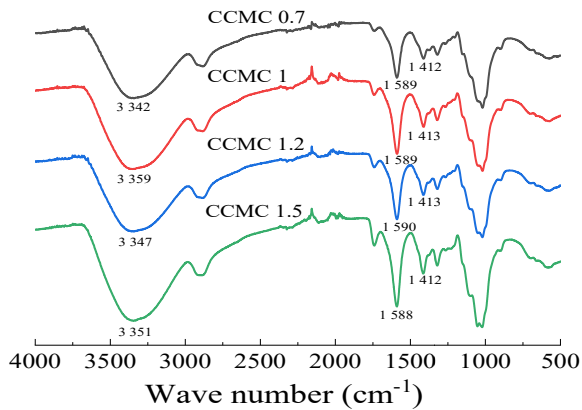


Fig.1 FTIR spectra of CCMCs with different degrees of carboxyl substitution

The morphologies of CCMCs were observed by SEM (Fig. 2), and the surface of CCMCs showed a spherical and porous structure, and became more and more rough and had more fold structures with the increase of carboxyl substitution degrees, indicating that CCMCs exposed more reactive sites after etheration and which would improve the adsorption capacity for pollutant. The specific surface area of CCMC with different carboxyl substitution degrees was shown in Table 2.1. The specific surface area of CCMCs with different carboxyl substitution degrees were similar, and CCMC 1.2 presented the largest specific surface area ( $1.005\text{m}^2/\text{g}$ ).

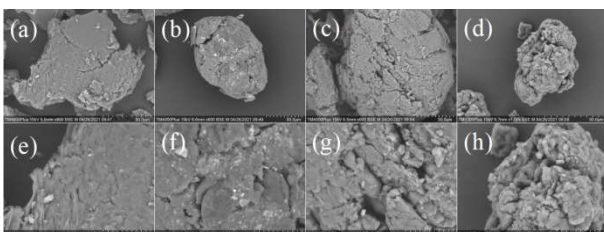


Fig.2 SEM images of CCMC with different degrees of carboxyl substitution: (a) CCMC 0.7 (50  $\mu\text{m}$ ), (b) CCMC 1 (50  $\mu\text{m}$ ), (c) CCMC 1.2 (50  $\mu\text{m}$ ), (d) CCMC 1.5 (50  $\mu\text{m}$ ), (e) CCMC 0.7 (20  $\mu\text{m}$ ), (f) CCMC 1 (20  $\mu\text{m}$ ), (g) CCMC 1.2 (20  $\mu\text{m}$ ), (h) CCMC 1.5 (20  $\mu\text{m}$ )

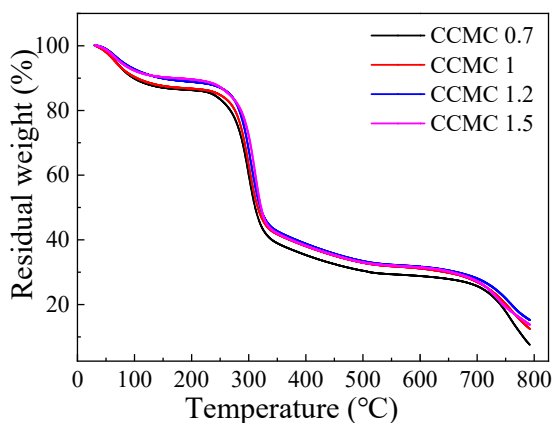


Fig. 3. Thermogravimetric analysis of CCMC

The thermogravimetric analysis was utilized to investigate the thermal stability of CCMCs as shown in Fig. 3. From 20°C to 110°C, the mass of CCMC was mainly ascribed to the volatilization of residual water in the adsorbent. From 230°C to 300°C, the carbon skeleton in the CCMCs carbonized, and oxygen-containing functional groups such as hydroxyl and carboxylic groups were oxidized and decomposed into carbon dioxide and water vapor, resulting in the rapid declining of mass. With the increase of the degree of substitution, the thermal stability of CCMCs were slightly enhanced. After 300°C, the mass slowly decreases and tends to equilibrium. CCMCs remain approximately 25% of the original mass when the temperature reached 700°C.

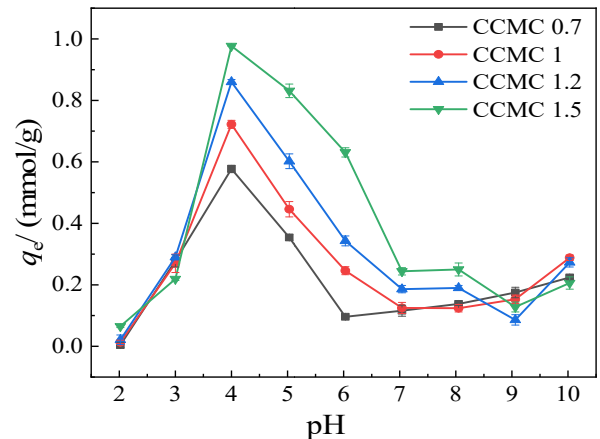


Fig. 5. Adsorption isotherms of CCMC for CIP at pH 4.0

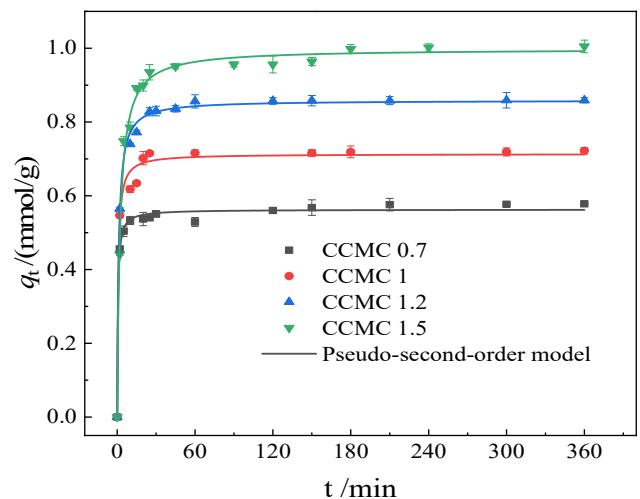


Fig. 6. Adsorption kinetics CCMC for CIP

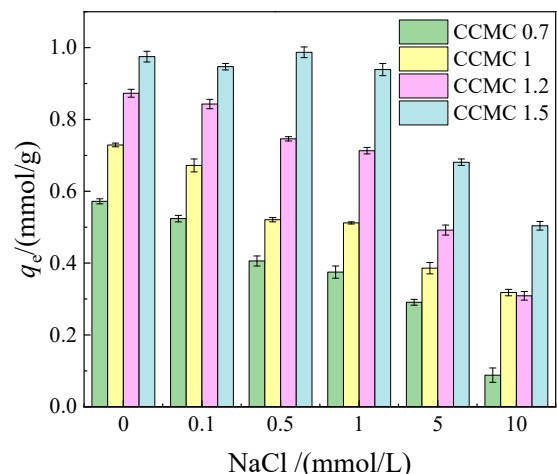


Fig. 7. Effect of NaCl concentration on CCMCs adsorption of CIP

Table 2 Fitting parameters of adsorption isotherms model

Adsorbent	$q_{max,exp}$ (mmol/g)	Langmuir model			Freundlich model		
		$q_m$ (mmol/g)	$K_L$ (L/mmol)	$R^2$	$K_F$	$n$	$R^2$
CCMC 0.7	0.652	1.439	5.729	0.958	2.558	1.429	0.893
CCMC 1	0.950	2.358	7.061	0.957	5.682	1.322	0.875
CCMC 1.2	1.123	2.432	12.239	0.984	7.703	1.391	0.938
CCMC 1.5	1.245	2.821	15.764	0.972	11.275	1.366	0.912

Table 3. Fitting parameters of adsorption kinetics of CIP to CCMC

Adsorbent	$q_{m,exp}$ (mmol/g)	Pseudo-first-order model			Pseudo-second-order model		
		$q_e$ (mmol/g)	$k_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_e$ (mmol/g)	$k_2$ ( $\text{g}/(\text{mmol}\cdot\text{min})$ )	$R^2$
CCMC 0.7	0.578	0.551	0.830	0.981	0.563	3.448	0.993
CCMC 1	0.722	0.696	0.768	0.969	0.713	1.988	0.985
CCMC 1.2	0.859	0.833	0.557	0.975	0.859	1.027	0.996
CCMC 1.5	1.005	0.952	0.278	0.972	0.998	0.458	0.992

### Adsorption performance and mechanisms

**pH effect:** Solution pH usually had an evident effect on the adsorption process because it can change the surface charges of adsorbent and pollutants. As shown in Fig. 4, CCMCs with different carboxyl substitution degrees showed a similar trend in the adsorptive removal of CIP. The adsorption capacity of CIP was improved with the increase of carboxyl substitution degrees.

The CIP uptakes increased with the increase of pH and then rapidly decreased, and the maximal CIP uptakes occurred at the initial pH 4.0. The maximum adsorption capacity of CCMC 1.5 was 0.977 mmol/g at pH 4.0. Under the acidic conditions, the higher adsorption capacity were ascribed to the electrostatic attractions between protonated amine groups of CIP and the carboxyl groups of CCMCs, and the hydrogen bonding interactions between the carboxyl group, the hydroxyl group and amine groups. At the neutral and alkaline conditions, the adsorption capacity of CIP decreased due to electrostatic repulsion, which also indicates that the electrostatic adsorption are major interaction in adsorption of CIP by CCMCs.

**Adsorption isotherms:** The adsorption capacity of CIP on CCMCs were improved with the initial CIP concentration increased as shown in Fig. 5. Langmuir and Freundlich adsorption isothermal models were used to simulate the isothermal adsorption dates, respectively, and the fitting parameters related to model are shown in Table 2. The correlation coefficients of Langmuir model were higher than Freundlich model, demonstrating that the adsorption process was monolayer adsorption. The theoretical maximum adsorption capacity of CCMC1.5 for CIP was 2.821 mmol/g.

**Adsorption kinetics:** The adsorption speed of CIP on CCMCs were relatively fast, and reached the adsorption equilibrium in about 60 min (Fig. 6). The pseudo-first-order and pseudo-second-order kinetic models were used to fit the adsorption kinetic results, and the kinetic fitting parameters were shown in Table 3.

The adsorption of CIP on CCMCs was more consistent with the pseudo-second-order model, indicating that the adsorption process was mainly chemical adsorption. The adsorption effect of CCMC with different carboxyl substitutions on CIP were not proportional to the specific surface areas, which further confirms the chemisorption plays a major role in adsorption of CIP.

**Influence of coexisting inorganic salt:** NaCl, as a representative, was used to investigated the effect of inorganic salt on CIP by CCMCs as shown in Fig. 7. The adsorption capacity of CCMC for CIP decreased with the increase of NaCl concentration, which further proves that electrostatic adsorption is the main effect of CIP adsorption on CCMCs.

## CONCLUSION

CCMCs with different carboxyl substitution degrees (1:0.7, 1:1, 1:1.2, 1:1.5) were synthesized by crosslinking cellulose, in succession by etherification, and CCMCs adsorbents can efficient adsorptive removal of CIP. FTIR spectra analyses demonstrated that CCMCs had been successfully synthesized. According to SEM results, the surface of adsorbent from CCMC 0.7 to CCMC 1.5 became more and more rough, but the specific surface area did not increase with the increase of carboxyl substitution degree. The thermal stability of the adsorbent increased with the increase of carboxyl substitution degree. pH has a great effect on CIP adsorption by CCMC. The adsorption capacity increased first and then decreases with the increase of pH. The CIP adsorption capacity of CCMC reached the maximum at pH 4.0, and the adsorption mechanism included electrostatic adsorption and hydrogen bonding. With the increase of carboxyl substitution degree, the adsorption capacity of CCMC for CIP increased gradually. CCMC 1.5 showed the best adsorption capacity for CIP, with a maximum adsorption capacity of 0.977 mmol/g. The adsorption isotherm conformed to the Langmuir model, which indicated that monolayer adsorption plays a dominant role in CIP adsorption by CCMC. The adsorption of CIP on CCMCs was more consistent with the pseudo-second-order kinetic model, indicating that CCMC adsorbent is mainly chemisorption. The CIP adsorption capacity of CCMC decreased with the increase of NaCl concentration, which further proved that electrostatic adsorption is the main interaction in adsorbing of CIP by CCMC. This study indicated that CCMCs, as an efficient adsorbent, has significant application potentials in removal of antibiotics from water.

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