



## Modified adsorbent hydroxypropyl cellulose xanthate for removal of Cu<sup>2+</sup> and Ni<sup>2+</sup> from aqueous solution

Yongzhong Zhang<sup>a</sup>, Chengcheng Luo<sup>b</sup>, Hui Wang<sup>b,\*</sup>, Li Han<sup>b</sup>, Chongqing Wang<sup>b</sup>, Xuanmin Jie<sup>b</sup>, Yong Chen<sup>b</sup>

<sup>a</sup>School of Geosciences and Info-Physics, Central South University, Changsha 410083, Hunan, China, email: [liuwuhui1968@163.com](mailto:liuwuhui1968@163.com)

<sup>b</sup>Key Laboratory of Resources Chemistry of Nonferrous Metals, School of Chemistry and Chemical Engineering, Ministry of Education, Central South University, Changsha 410083, Hunan, China, emails: [ginoluo2011@163.com](mailto:ginoluo2011@163.com) (C. Luo), [huiwang1968@163.com](mailto:huiwang1968@163.com) (H. Wang), [179412502@qq.com](mailto:179412502@qq.com) (L. Han), [786252819@qq.com](mailto:786252819@qq.com) (C. Wang), [jxmerish@gmail.com](mailto:jxmerish@gmail.com) (X. Jie), [195073094@qq.com](mailto:195073094@qq.com) (Y. Chen)

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### ABSTRACT

A modified adsorbent, namely hydroxypropyl cellulose xanthate (HCX), was synthesized for removal of heavy metal ions from aqueous solution. HCX was prepared by introducing xanthogenated groups, and the sulfur group in HCX was confirmed by scanning electron microscope, Fourier Transform Infrared, nuclear magnetic resonance, and ultraviolet-visible spectra. The sulfur group plays a significant role in chelating with heavy metal ions. Adsorption of copper and nickel ions by HCX was conducted, and the factors of adsorption time, temperature, adsorbent dose, and pH value were investigated. The removal rate of copper and nickel ions were up to 98 and 83% under the optimum condition, respectively. Adsorption isotherms indicated that Langmuir isotherm model had a better linearity and the maximum adsorption capacities of copper and nickel ions were 126.58 and 114.29 mg g<sup>-1</sup> respectively, confirming that the affinity of metal ions onto sulfur-bearing groups was considerable.

*Keywords:* Hydroxypropyl cellulose xanthate; Xanthogenated groups; Adsorption; Heavy metal ions

### 1. Introduction

Heavy metals are widely used in various industries [1–3], and they have become a major threat to environment due to the undegradability and toxicity in living systems [4–8]. Numerous techniques have been developed for treating wastewater contaminated by heavy metal ions [9–12]. Conventional methods for removing heavy metal ions from aqueous solutions

include chemical precipitation, oxidation, electrochemical treatment, solvent extraction, adsorption, ion exchange and membrane filtration technologies, etc. [13–19]. While these methods maybe cost-effective or ineffective and low removal rate when the concentration of metal ions in solution are in the range of 1–100 mg L<sup>-1</sup> [20]. In recent years, adsorption technology is regarded as an attractive alternative for heavy metal ion removal from wastewater, and great efforts have been made to exploit new materials possessing properties such as low cost, high availability

\*Corresponding author.

as well as efficient production process [1]. Agricultural wastes as adsorbents have manifested outstanding capabilities for removal of metal ions [21–24]. The hydroxyl groups in biomass chain bond with other groups and show a high affinity for heavy metal ions [25,26].

Hydroxypropyl cellulose (HPC) is a partially hydroxypropyl-substituted cellulose, in which some of the hydroxyl groups in the repeating glucose units have been hydroxypropylated with propylene oxide forming  $-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_3$  groups. HPC often acts as an intermediate to synthesize other derivatives, and generally shows good reaction performance [27]. The introduction of hydroxypropyl groups into the cellulose backbone makes the macromolecules possess special properties, and this has found numerous applications in medicine, pharmacology, and membrane industry [28]. HPC, a rather heterogeneous polymer, is always used for emulsifying and thickening in non-dairy whipped topping [29], used as semipermeable membranes for drug delivery, and used in coating materials for reservoir or osmotic systems and excipients for matrix systems [30].

Most high molecular weight polysaccharides do not adsorb at the air/water interface [31]. However, HPC is a thick biopolymer having surface-active properties both at air/water and oil/water interfaces due to their mixed hydrophilic/hydrophobic structure [29,31]. G. Cavallaro and his coworkers studied the adsorption of thermosensitive polymer HPC onto the nanoclay surface in aqueous solution, and the adsorption equilibrium could explain the air/solution interface properties well [32]. Within this issue, HPC serving as a new synthetic material has a good solubility in water. It is easier to achieve a new environmental and high-efficiency adsorbent mainly for removal of heavy metal ions. The removal of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions in aqueous solution was investigated, and the potential adsorption capacity of HCX in single system was determined.

## 2. Materials and methods

### 2.1. Materials

HPC powder used as raw material was purchased from Hebei Barilla biological Co., Ltd, China. All used chemicals in this work were of analytical reagent grade. The standard solution of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  were prepared by dissolving  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in distilled water, respectively.

### 2.2. Methods

#### 2.2.1. Characterization of adsorbent

Surface morphology analysis of the adsorbent was carried out using a scanning electronic microscope (SEM) (MIRA 3, TESCAN). Fourier Transform Infrared (FT-IR) spectra were recorded using KBr pellets with a NEXUS670 396 (Thermo Fisher Scientific) FT-IR spectrometer over the wavelength range  $400\text{--}4,000\text{ cm}^{-1}$ . Ultraviolet spectra were recorded with an ultraviolet-visible (UV-vis) spectrophotometer. The  $^1\text{H}$  nuclear magnetic resonance (NMR) spectra were recorded with 5-mm tubes in  $\text{D}_2\text{O}$  solution using AVANCE III HD 500 spectrometers. Sulfur content was measured by infrared carbon-sulfur analyzer (LECO, CS844).

#### 2.2.2. Standard curve of copper ion and nickel ion

The concentration of heavy metal ions was measured by UV-vis spectra with UV-2450 spectrophotometer (Shimadzu Corporation, Japan) in pH 9–11 for  $\text{Cu}^{2+}$  and alkaline medium for  $\text{Ni}^{2+}$ . The content of  $\text{Cu}^{2+}$  was recorded in the range of  $0.01\text{--}0.15\text{ mg L}^{-1}$  by UV spectrophotometric method at 440 nm, and  $\text{Ni}^{2+}$  was recorded in the range of  $0.5\text{--}2\text{ mg L}^{-1}$  at 470 nm. The standard curves are exhibited below in Fig. 1. Linear correlation coefficient  $R^2$  could be as high as 0.99988 and 0.99971 for  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ , respectively.

### 2.3. Synthesis of hydroxypropyl cellulose xanthate (HCX)

HPC (3 g) was alkalinized by 20 wt.% NaOH solution (60 mL) in a round-bottom flask under room temperature for 1 h. After this step, another 40 mL of NaOH solution was mixed into the slurry and then 3 mL of  $\text{CS}_2$  was added dropwise at  $30^\circ\text{C}$  for 4 h, and stirring was needed for every stage. Afterward, 5 wt.%  $\text{MgSO}_4$  solution (100 mL) was added into the flask for about 15 min to generate cellulose xanthate magnesium which is more stable than cellulose xanthate sodium [33]. After that, 300 mL of absolute ethyl alcohol was poured into the suspension, and the product was separated. After filtering the alcohol, the product was dissolved in about 10 mL of distilled water for dispersing agglomerate product. Purification of HCX by ethyl alcohol was repeated several times. Subsequently, the product was dried in vacuum oven at  $40^\circ\text{C}$  for 8 h. The mass obtained of HCX was 3.2 g and the sulfur content was recorded as 10.1%. The treatment procedure for preparation of HCX is illustrated in Fig. 2.

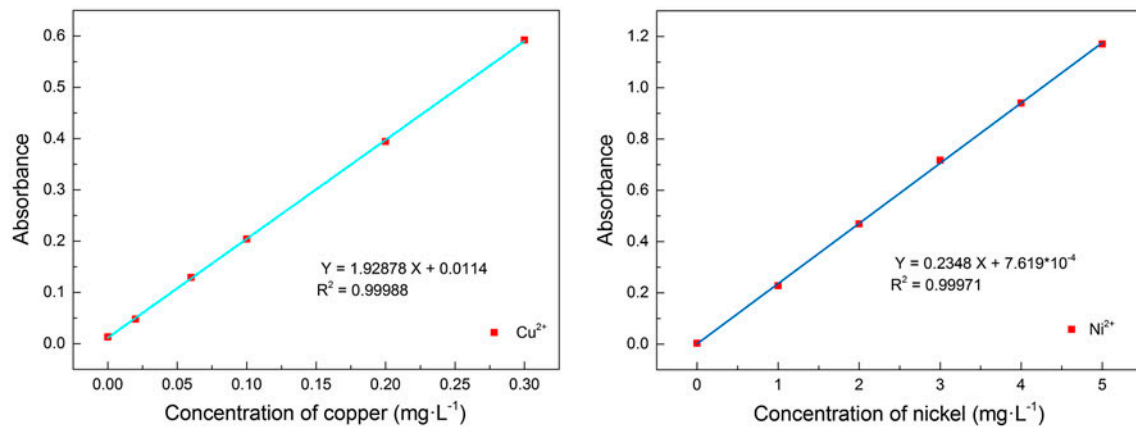


Fig. 1. Standard curves of Cu(II) and Ni(II).

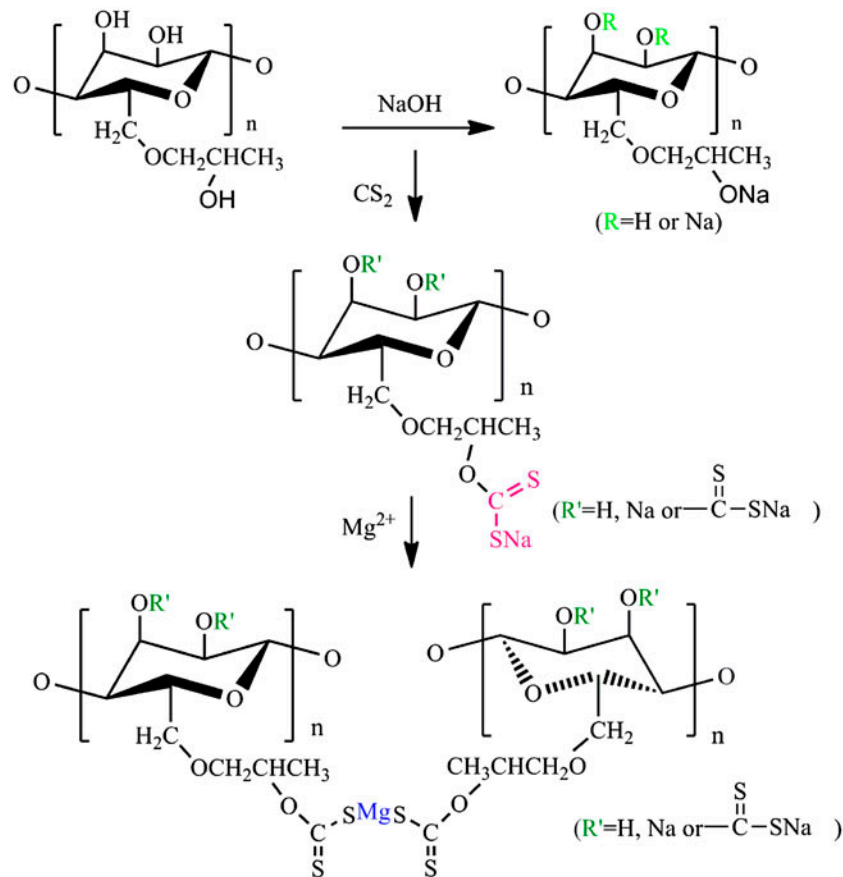


Fig. 2. Synthetic principles of Hydroxypropyl Cellulose Xanthate (HCX).

#### 2.4. Heavy metal ions removal

The adsorption experiments were carried with aqueous solutions of Cu<sup>2+</sup> and Ni<sup>2+</sup> ions. The initial concentration of Cu<sup>2+</sup> was 931.2 mg L<sup>-1</sup> and Ni<sup>2+</sup> was 954.1 mg L<sup>-1</sup> before adsorption. The pH value of

solution was adjusted with dilute H<sub>2</sub>SO<sub>4</sub> and NaOH solution. The solution containing heavy metal ion was contacted with an accurately weighed amount of dried HCX in a conical flask with glass lid, and then kept under continuous oscillation in water-bathing thermostatic oscillator. After an appropriate time, the mixture

was centrifuged and the residual concentration of heavy metal ion in liquid phase was measured. Adsorption capacity and removal rate were evaluated by the following Eqs. (1) and (2):

$$q_e = \frac{(c_0 - c_1) \times V}{m} \quad (1)$$

$$R = \frac{(c_0 - c_1)}{c_0} \times 100\% \quad (2)$$

where  $q_e$  and  $R$  are the adsorption capacity and removal rate, respectively;  $c_0$  and  $c_1$  represent the initial and the residual heavy metal ion concentrations ( $\text{mg L}^{-1}$ ), respectively.  $V$  is the volume of solution (mL), and  $m$  is the amount of HCX (g).

### 3. Results and discussion

#### 3.1 Characterization

The SEM photographs of HPC and HCX are shown in Fig. 3. It is observed that the HPC consists of particles with diameter of 10–15  $\mu\text{m}$  with a distinct smooth-faced surface due to the strong intra-molecular hydrogen bonds and the stereo-hindrance effect [34,35]. HCX possesses a porous structure on account of the corrosion by alkali solution and the xanthogenation by  $\text{CS}_2$ , which hamper the formation of inter- and intra-molecular hydrogen bonds. The porous structure would remarkably increase the available surface area of the adsorbent, giving rise to the enhancement of adsorption capacity.

The FT-IR spectra were recorded as a qualitative analysis to determine the main functional groups in the HPC and HCX. As presented in Fig. 4, the broad

absorption band at  $3,436 \text{ cm}^{-1}$  corresponded to the characteristic stretching vibration of  $-\text{OH}$ , and the peak at  $2,924$  and  $2,854 \text{ cm}^{-1}$  corresponded to the C–H tensile vibration. The sharp band at  $1,451 \text{ cm}^{-1}$  corresponded to the deformation vibration of  $-\text{CH}_2$  group [36], and the appearance of an absorption band located at  $1,155 \text{ cm}^{-1}$  was attributed to C–O–C stretching vibration of cellulose [37]. Some distinct changes were noted after xanthation of HPC. In addition, the adsorption peak at  $1,646 \text{ cm}^{-1}$  varied after the HPC treated by  $\text{CS}_2$ , and the presence of sulfur groups in the HCX had been identified by the appearance of new peaks at  $1,104 \text{ cm}^{-1}$  which corresponded to the vibration of C=S group [8].

Several reports pointed out that the cellulose xanthate was determined by measuring the ultraviolet absorbance at 303 nm [38–40]. Fig. 4 shows the absorption spectrum of cellulose xanthate in distilled water in the range 210–470 nm, where absorption maximum at 303 nm was observed. And it is obviously different from the spectrum of the HPC, for there was an intense peak at 223 nm. Aqueous solutions of HCX are unstable and easy to decompose. This instability is enhanced by decreasing hydroxide ion concentration and increasing temperature [38]. It is, therefore, advisable to keep the solution cold and read the absorbance of the solution as soon as possible after ion exchange.

The NMR spectra were seen by Fig. 5, and the proton chemical shifts of HCX were extremely different with HPC due to the treatment of  $\text{CS}_2$ . The reduplicative units in HPC were destroyed to be unordered, and thus the peaks in HCX were more tanglesome. The active hydrogen in hydroxyl will not be detected in  $\text{D}_2\text{O}$ , and only the signal peak of alkyl group and backbones in the spectra are observed.

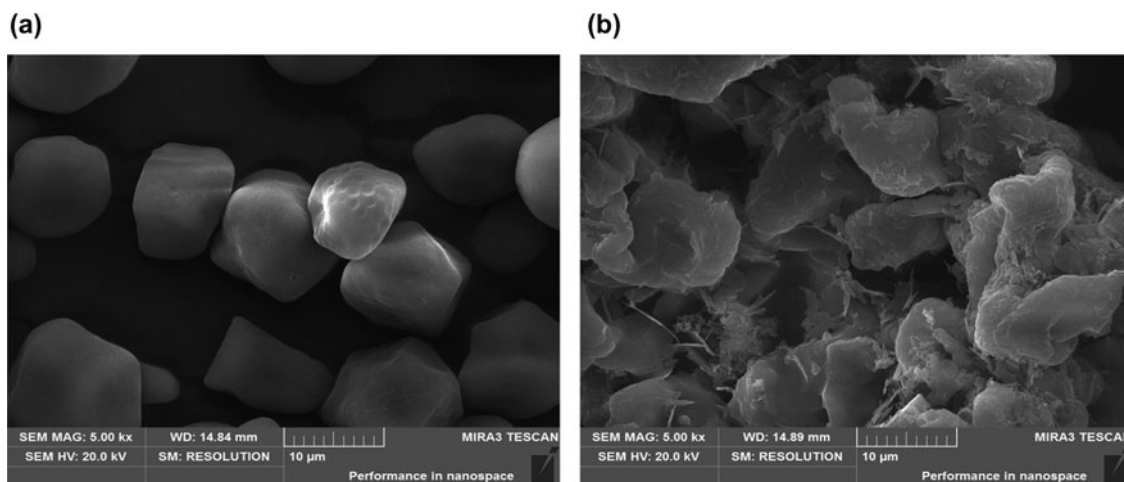


Fig. 3. SEM images of (a) HPC and (b) HCX.

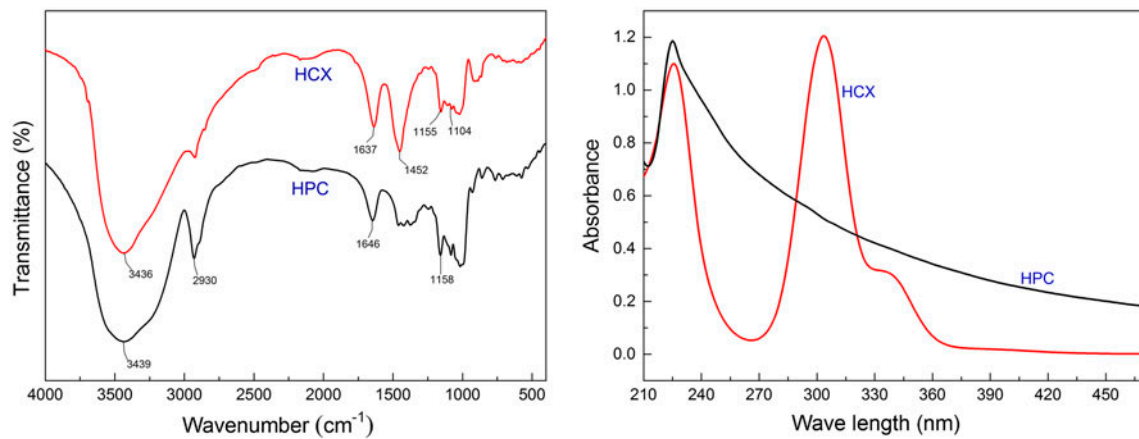


Fig. 4. FT-IR spectra and UV absorption spectra of HPC and HCX.

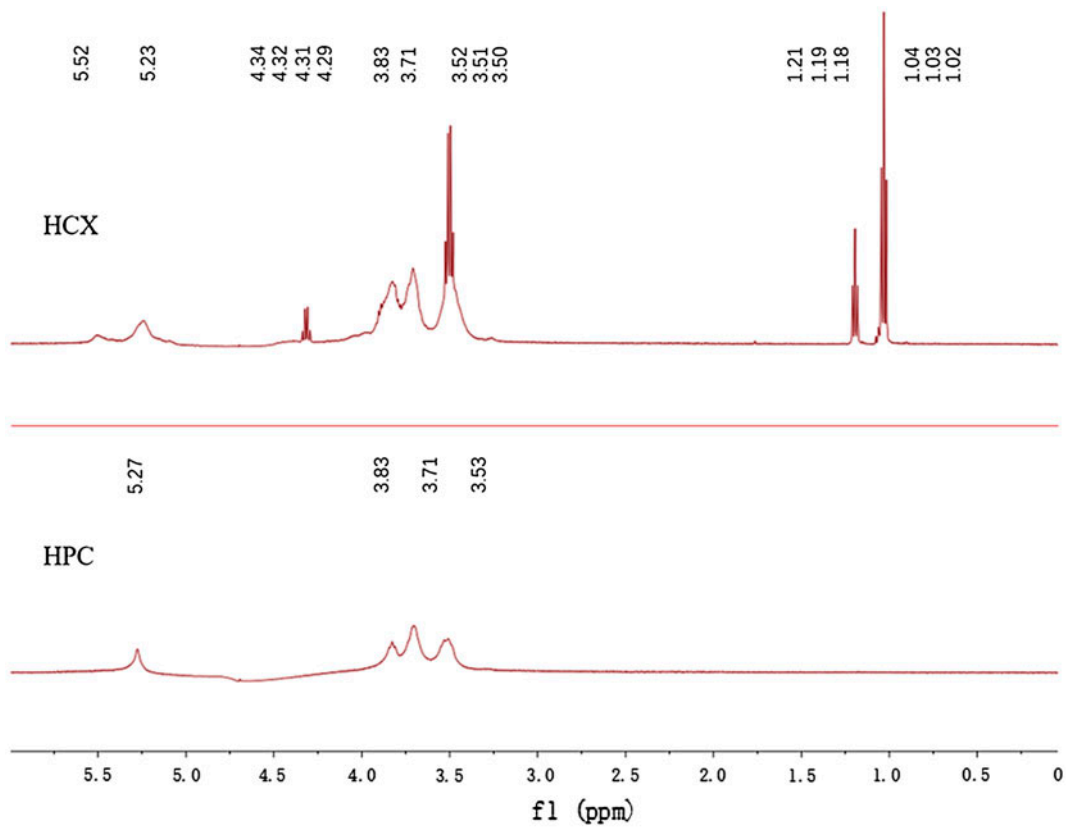


Fig. 5. The <sup>1</sup>H NMR spectra of HCX and HPC in D<sub>2</sub>O solution. (The signal peak of D<sub>2</sub>O was suppressed for featuring the peak of alkyl group and backbones).

### 3.2. Treatment of wastewater containing heavy metal ions

#### 3.2.1. Effect of HCX consumption

The consumption of HCX for removal of Cu<sup>2+</sup> and Ni<sup>2+</sup> was investigated from 0.05 to 0.3 g 25 mL Cu<sup>2+</sup>

solution (931.2 mg L<sup>-1</sup>) while Ni<sup>2+</sup> solution (954.1 mg L<sup>-1</sup>) was treated the same way. The pH value of Cu<sup>2+</sup> solution was adjusted to about five while the pH value of Ni<sup>2+</sup> solution was around six, oscillating under 30°C for 30 min. Then, centrifugation



was needed and metal ion concentration in the supernatant liquor was measured by UV–vis spectra. According to the principle of equivalent exchange ions, the theoretical amount of HCX is determined by the following Eq. (3) [41]:

$$M(\text{HCX}) = 6.412 \times V \times \rho(\text{Me}^{n+}) \times n / [M \times w(\text{S})] \quad (3)$$

where  $V$  is the volume of heavy metal ion solution (L),  $\rho(\text{Me}^{n+})$  is the concentration of heavy metal ions ( $\text{g L}^{-1}$ ),  $n$  is the metal ion valence, and  $M$  is the relative atomic mass,  $w(\text{S})$  is sulfur content which was recorded as 10.1%. Theoretical amount gives a basis for the consumption of HCX.

The effect of HCX consumption on  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  removal was demonstrated in Fig. 6a. The concentration of heavy metal ions dropped obviously at first stage with the increment of HCX dose. This may be attributed to chemical modification which was expected to increase the binding sites in the surface area of the adsorbent and enhanced the adsorption capacity of HCX [28]. The residual heavy metal ions in aqueous solution no longer reduced until the adsorbent exceeded 0.2 g (about four times the theoretical amount), which indicated that adsorption had reached saturation point. At higher dosage, the adsorption capacity was low, and this may be due to overlapping of adsorption sites resulting in overcrowding of adsorbent particles. The residual concentration of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  was 0.019–0.166  $\text{g L}^{-1}$  in the end, and removal rate could reach 98 and 83%, respectively.

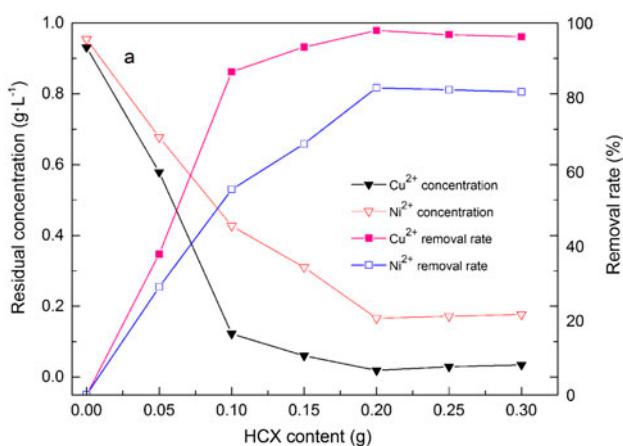


Fig. 6a. Effect of HCX content on the adsorption of Cu(II) and Ni(II). Conditions: contact time 30 min, solution pH 5.0 for Cu(II) and pH 6.0 for Ni(II).

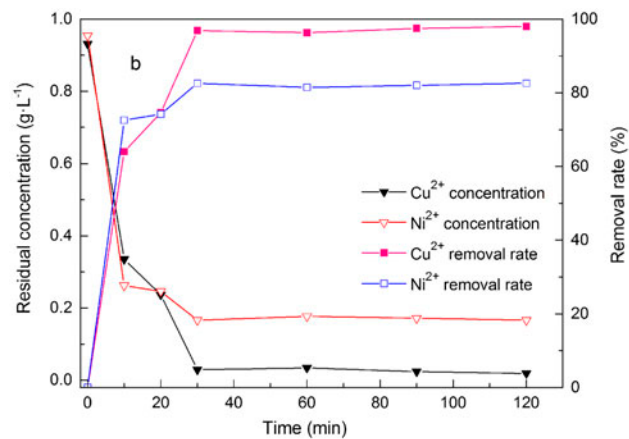


Fig. 6b. Effect of contact time on the adsorption of Cu(II) and Ni(II). Conditions: adsorbent dose 0.2 g, solution pH 5.0 for Cu(II) and pH 6.0 for Ni(II).

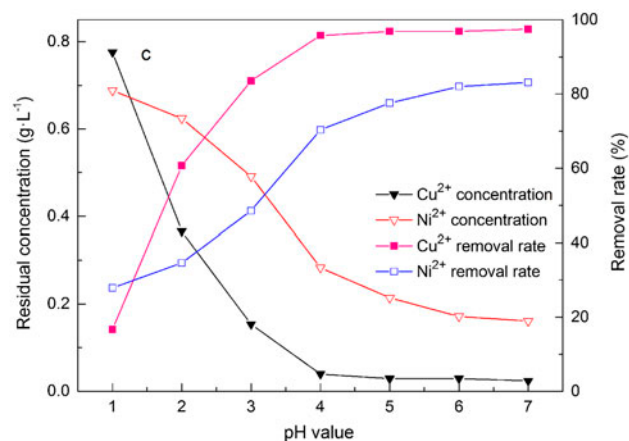


Fig. 6c. Effect of pH on adsorption of Cu(II) and Ni(II). Conditions: contact time 30 min, adsorbent dose 0.2 g.

### 3.2.2. Effect of time

To further assess the effect of time on the adsorption efficiency, general procedure was performed for 25 mL of solution ( $\text{Cu}^{2+} = 931.2 \text{ mg L}^{-1}$ ,  $\text{Ni}^{2+} = 954.1 \text{ mg L}^{-1}$ ) by varying the time from 10 to 120 min. The adsorption process was carried out at pH 5 for  $\text{Cu}^{2+}$  and 6 for  $\text{Ni}^{2+}$  with oscillating temperature 30°C. It was found that HCX chelated with metal ions rapidly in the primary stage and 64% of  $\text{Cu}^{2+}$  and 72.5% of  $\text{Ni}^{2+}$  were removed within 10 min. According to Fig. 6b, the concentration of HCX slightly decreased with time, resulting in the decreased collision efficiency between molecules[42]. With time, a decrement of active sites was accompanied by a moderate decrease in metal ions, and the curve flattened out correspondingly.

### 3.2.3. Effect of pH

The metal speciation and ionization were affected by the pH value as well as the surface charge of the adsorbent. Thus, the metal ion adsorption was highly dependent on suitable pH value [43,44]. Fig. 6c manifested the result of heavy metal ion removal affected by the pH value of the solution. As it can be observed, the removal rate increased gradually until pH value rose to about 5, and then remained unchanged for both  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ . At low pH, the  $\text{H}^+$  competition with heavy metal ions limits the uptake efficiency [45]. The higher pH value enhanced the removal rate of heavy metal ions, due to the ionization of xanthogenic acid groups [46]. As a result, the HPC xanthate (HCX) obtained the maximum adsorption capacity of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  at pH near 5 and 6, respectively.

### 3.2.4. Effect of temperature

The effect of temperature on adsorption of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  by HCX was studied using  $1 \text{ g L}^{-1}$  initial metal concentration at 30, 40, and  $50^\circ\text{C}$ . As presented in Fig. 7, it was found that the adsorption capacity decreased with increasing temperature. It indicated that the adsorption process was exothermic in nature. The thermodynamic parameters such as change in free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ) were calculated by the following equations [56,57]:

$$\Delta G = -RT \ln K_c \quad (4)$$

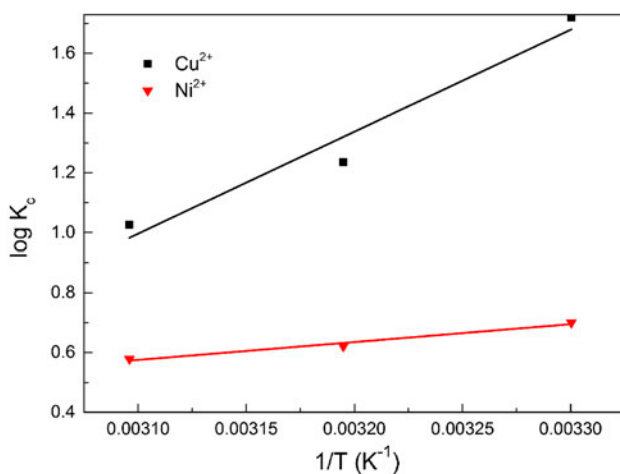


Fig. 7. Plot of  $\log K_c$  vs.  $1/T$  for estimation of thermodynamic parameter.

$$K_c = \frac{C_{Ac}}{C_e} \quad (5)$$

$$\log K_c = \frac{\Delta S}{2.30R} - \frac{\Delta H}{2.303RT} \quad (6)$$

where  $R$  is the gas constant,  $T$  is the temperature (In  $K$ ),  $K_c$  is the equilibrium constant,  $C_{Ac}$  is the equilibrium concentration of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  on adsorbent ( $\text{mg L}^{-1}$ ), and  $C_e$  is the equilibrium concentration of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  in solution ( $\text{mg L}^{-1}$ ).

The values of  $\Delta H$  and  $\Delta S$  were calculated from the slope and intercept of the linear plots of  $\log K_c$  vs.  $1/T$ . The results are presented in Table 1. The negative values of  $\Delta G$  indicated the spontaneous nature of adsorption. The  $\Delta G$  values decreased with increase in temperature, indicating lesser adsorption capacity at higher temperatures [49]. The negative values of  $\Delta H$  and  $\Delta S$  confirmed the exothermic nature and the decreased randomness at the solid/solute interface during the adsorption of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ , respectively.

### 3.3. Adsorption equilibrium

The Langmuir and the Freundlich adsorption models were calculated for better understanding the kinetics of adsorption of heavy metal ions [47].

#### 3.3.1. Langmuir model

The main objective of Langmuir adsorption model was to estimate the capacity of uptaking metal ions. The linear form of the Langmuir isotherm is described by Eq. (7) [48]:

$$C_e/q_e = 1/k_L q_m + C_e/q_m \quad (7)$$

where  $C_e$  and  $q_e$  are the equilibrium metal ion concentration in the solution ( $\text{mg L}^{-1}$ ) and the equilibrium metal ion concentration on the adsorbent ( $\text{mg g}^{-1}$ ),  $k_L$  ( $\text{L mg}^{-1}$ ) is the adsorption affinity constant which is connected to the energy of adsorption and  $q_m$  is the Langmuir saturated adsorption capacity of the adsorbent.

The enumerative Langmuir and affinity constants are shown in Table 1. A straight line between  $C_e$  and  $C_e/q_e$  was plotted with a slope of  $1/q_m$  and an intercept of  $1/k_L q_m$ , which are shown in Figs. 8a and 8b. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter  $R_L$ . It is calculated by [35]:

Table 1  
Thermodynamic parameters for the adsorption of Cu(II) and Ni(II) ions onto HCX

Metal	Temperature (°C)	Thermodynamics			$R^2$
		$\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	
Cu(II)	30	-9.98156	-65.344	-183.254	0.915
	40	-7.40266			
	50	-6.34475			
Ni(II)	30	-4.06142	-11.443	-24.424	0.957
	40	-3.72466			
	50	-3.5764			

$$R_L = \frac{1}{1 + k_L M c_0}$$

$$(8) \quad \ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (9)$$

where  $c_0$  (mmol L<sup>-1</sup>) is the highest initial metal ion concentration,  $M$  is the molar mass of metal ions.

The values of  $R_L$  calculated are incorporated in Table 2. As the values of  $R_L$  are between 0 and 1, the adsorption system is favorable. And  $R_L = 1$  represents linear adsorption, while the adsorption process is irreversible if  $R_L = 0$  [50]. The dimensionless parameter  $R_L$  remained between 0.787 and 0.954 ( $0 < R_L < 1$ ) consistent with the requirement for a favorable adsorption process.

### 3.3.2. Freundlich model

The Freundlich isotherm model is used to estimate the adsorption capacity (mg g<sup>-1</sup>) and adsorption intensity. Its equation model can be expressed as Eq. (9). Fig. 9 showed the relationship between  $\ln C_e$  and  $\ln q_e$  which was linear with a slope of  $1/n$  and an intercept of  $\ln k_F$ .

where  $k_F$  is indicative of adsorption coefficient;  $n$  represents the adsorption intensity of Cu<sup>2+</sup> and Ni<sup>2+</sup> toward HCX.

The adsorption isotherm parameters evaluated for Cu<sup>2+</sup> and Ni<sup>2+</sup> are given in Table 2. The order for removal efficiency in the case of aqueous solution is: Cu<sup>2+</sup> > Ni<sup>2+</sup>. The differences in removal efficiency could be primarily due to their different affinity between various metal ions and cellulose xanthate salt, and the different mean adsorption energy that can influence the ionic states of the metal ions [51,52]. According to the results, it could be seen that the correlation coefficient ( $R^2$ ) value of Langmuir model was closer to one compared with Freundlich model, revealing the linear Langmuir isotherm model had a better linearity. The applicability of the Langmuir isotherm suggested that the sorption was uniform and homogeneous as to the surface of the adsorbent as well as energy, resulting in the formation of a monolayer

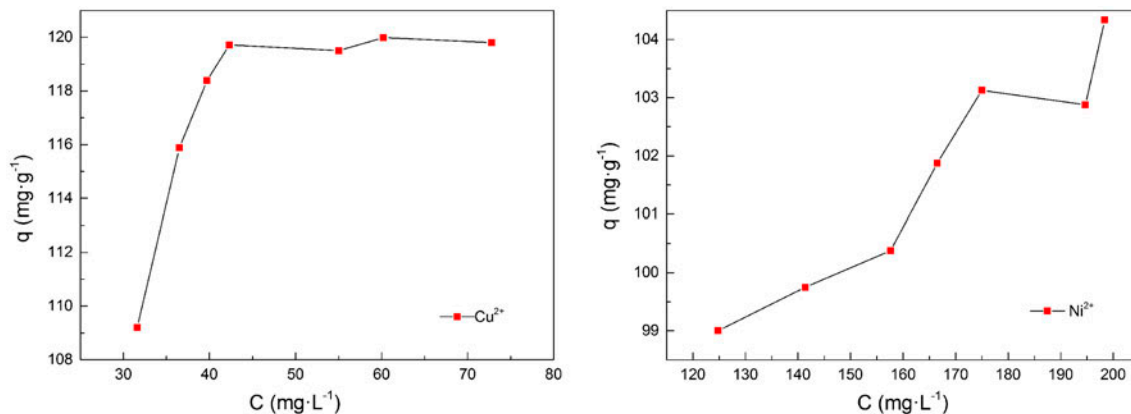


Fig. 8a. Adsorption isotherms of Cu(II) and Ni(II) for adsorption by HCX.



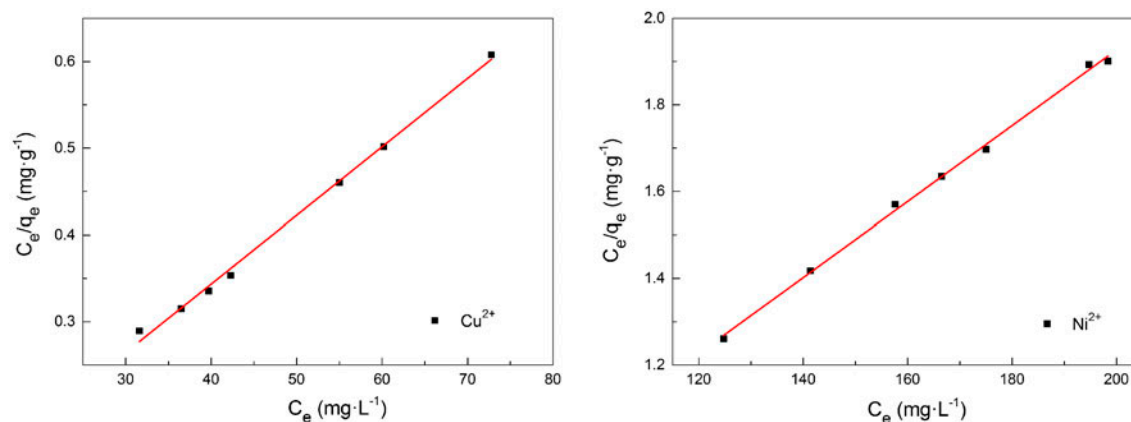


Fig. 8b. Linearized forms of Langmuir model for adsorption of Cu(II) and Ni(II) by HCX.

Table 2

Parameters of Langmuir and Freundlich isotherm constants for sorption of copper(II) and nickel(II) ions onto HCX at 30°C for 30 min

	Langmuir adsorption isotherm				Freundlich adsorption isotherm		
	$q_m$ (mg g <sup>-1</sup> )	$k_L$ (L mg <sup>-1</sup> )	$R^2$	$R_L$	$k_F$	$1/n$	$R^2$
Cu <sup>2+</sup>	126.58	0.29	0.996	0.787	99.11	0.045	0.90
Ni <sup>2+</sup>	114.29	0.05	0.997	0.954	58.02	0.11	0.88

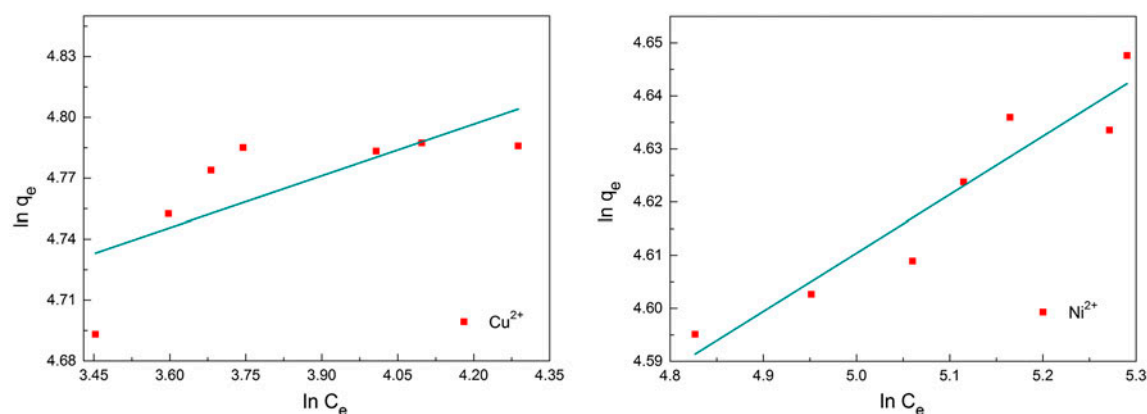


Fig. 9. Freundlich adsorption isotherms of Cu(II) and Ni(II) by HCX in single system.

coverage of Cu<sup>2+</sup> and Ni<sup>2+</sup>. Modified HCX possesses the characteristic of strong adsorption capacity. Comparison of HCX and modified HCX are showed in Table 3.

### 3.4. Adsorption kinetics

In order to better understand the kinetics of adsorption of heavy metal ions on HCX, it was stud-

ied for the efficiency of adsorption [45]. Kinetics data are modeled using pseudo-first-order model and pseudo-second-order model, the models were given by Eqs. (10) and (11). The pseudo-first-order equation was utilized to plot the data as  $\ln(q_e - q_t)$  against  $t$  and pseudo-second-order equation was  $t/q_t$  against  $t$ . The sample plot for HCX at 30°C for Cu(II) and Ni(II) ions is given in Fig. 10 and related parameters are shown in Table 4:

Table 3

Comparison of hydroxypropyl cellulose xanthate and modified hydroxypropyl cellulose xanthate on the study of metal ions adsorption

Cellulose xanthate	Metals	Adsorption capacities (mg g <sup>-1</sup> )	pH	Temperature (°C)
HCX	Cu(II), Ni(II)	126.58, 114.29	5.0–6.0	30
Insoluble bagasse xanthate [53]	Cu(II)	26.9	5.0 ± 0.1	18–21
Insoluble wood xanthate [53]	Cu(II)	27.8	5.0 ± 0.1	18–21
Orange peel xanthate [44]	Cu(II), Ni(II)	77.60, 15.45	5.0–5.5	25
Eichhornia crassipes root cellulose xanthate [54]	Cu(II)	98.37	4.5	25 ± 1
Modified sawdust xanthate [35]	Cu(II), Ni(II)	64.58, 40.86	6.0 ± 0.1	25
Xanthate-modified magnetic chitosan [8]	Cu(II)	34.5	6.0	30

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (10)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (11)$$

where  $k_1$ ,  $k_2$ ,  $q_e$ , and  $q_t$  are the pseudo-first-order adsorption rate constant (min<sup>-1</sup>), the pseudo-second-order rate constant (g mg<sup>-1</sup> min<sup>-1</sup>), the adsorption amount by per unit adsorbent at equilibrium and at time  $t$  (mg g<sup>-1</sup>), respectively.

From Fig. 10, it is obvious that the adsorption process could be well fitted by pseudo-second-order equation. This suggests the chemical adsorption is the rate limiting step. The mechanism involved in the adsorption of Cu<sup>2+</sup> and Ni<sup>2+</sup> onto HCX may be partly a result of the ion exchange followed by complexation. The HCX can bind transition metal ions by the formation of the coordination complex in which four sulfur atoms are associated with one divalent metal ion or two sulfur atoms associated with one divalent metal

ion [2,42]. When cellulose xanthogenate dissolved in water, the active group could be hydrolyzed and ionized and was turned into xanthated ion in the end. The negative charge of S atom in  $-\text{O}-\text{C}(=\text{S})-\text{S}^-$  disperses in a large space, thus displaying a negative electric field in a relative wide scope. So it could capture the cation, and tended to form the low solubility chelate [55].

Table 4

Pseudo-first-order and pseudo-second-order for the adsorption of metal ions on HCX at 30°C

Metal ions	Cu(II) ion	Ni(II) ion
First-order kinetics $\ln(q_e - q_t) = \ln q_e - k_1 t$		
$k_1 (\times 10^{-2} \text{ min}^{-1})$	5.38	3.86
$R^2$	0.979	0.965
Second-order kinetics $t/q_t = 1/k_2 q_e^2 + t/q_e$		
$k_2 (\times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1})$	1.6	6.5
$R^2$	0.997	0.999

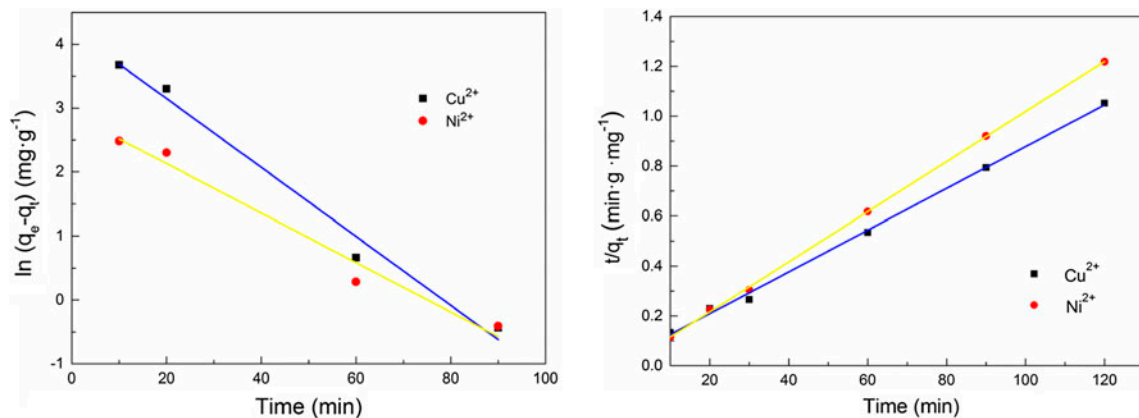


Fig. 10. Pseudo-first-order and pseudo-second-order kinetic model plots for adsorption of Cu(II) and Ni(II).

Because copper and nickel ions belong to transition metals, they have empty orbitals that can be occupied by extra electrons of S in HCX [42].

#### 4. Conclusions

In this work, a new adsorbent HCX was synthesized and applied for adsorption of heavy metal ions. The modified cellulose demonstrated distinctive adsorption capability of copper and nickel ions. The optimum pH value in adsorption was about 5 and 6 for  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ . The adsorption equilibrium was achieved at 30 min and the adsorption saturation point was reached using 8 g HCX per liter heavy metal ion solution. The removal rate of copper and nickel ions were up to 98 and 83% under optimum conditions. Langmuir model correlated better with the adsorption mechanism. The maximum adsorption capacity of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  were 126.58 and 114.29  $\text{mg g}^{-1}$ , respectively. Kinetics studies indicated that the adsorption reaction followed pseudo-second-order model, and an ion exchange reaction followed by complexation mechanism might be involved in the adsorption. The results confirmed the potential of HCX as an effective adsorbent for the removal of heavy metal ions.

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