Facile Preparation of Carbon Nanotubes based Carboxymethyl Chitosan Nanocomposites through Combination of Mussel Inspired Chemistry and Michael Addition Reaction: Characterization and Improved Cu²⁺ Removal Capability

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Abstract

The adsorption removal of heavy metal ions from aqueous solution using polymer nanocomposites has attracted great interest because of their advantages from both nanomaterials and polymers. In this work, a facile and novel method has been developed for surface modification of multi-walled carbon nanotubes (CNT) with carboxymethyl chitosan via combination of mussel inspired chemistry and Michael addition reaction. To obtain resultant CNT based chitosan nanocomposites (CNT-PDA-CS), pristine CNT were first coated with polydopamine (PDA) thin films through self polymerization of dopamine under alkaline aqueous solution. Then PDA modified CNT were further functionalized with carboxymethyl chitosan (CS) via Michael addition reaction. The successful preparation of CNT-PDA-CS nanocomposites was ascertained by a series of characterization techniques including transmission electron microscopy, Fourier transform infrared spectroscopy, thermal gravimetric analysis and X-ray photoelectron spectrometry. The utilization of the resultant CNT-PDA-CS for removal of Cu^{2+} from aqueous solution was also examined in this work. The results showed that CNT-PDA-CS exhibited obviously enhanced Cu^{2+} removal capability as compared with the unmodified CNT. **Considered the versatility of mussel inspired chemistry**, the method described in this work should be a general route for **fabricating highly** efficient adsorbents, which should be of great interest for environmental applications.

Key words: Carbon nanotubes; chitosan; mussel inspired chemistry; heavy metal ion removal; Michael addition reaction

1. Introduction

In recent years, environmental pollution by heavy metal ions has become one of the most serious environmental problems and have drawn more and more attentions.[1] These heavy metal ions are non-biodegradable and can exist for a long time in natural environment, thus resulting in long-term risk to ecosystem and human beings. Therefore, removal of these toxic heavy metal ions from industrial effluents prior to their discharge is of particular importance. Among these heavy metal ions, the copper ions should be the most typical ones because they were involved in many industrial processes, such as electroplating, paint, electrical, fertilizer, wood manufacturing and pigment industries.[2-5] Previously, a number of methods, including chemical precipitation, ion exchange, liquid-liquid extraction, electrodialysis, biosorption have been developed to remove these toxic metal ions.[6-11] Much attention has been focused on the removal of Cu^{2+} ions by adsorption because of its simplicity, relative low-cost, effective and flexible in design and operation.[12-14] Up to now, numerous adsorbents including carbon nanotubes (CNT), magnetic nanoparticles, graphene oxides, silica nanoparticles and so on have been examined as adsorbents due to their small size and high specific surface area.[15-25] However, most of these nanomaterials based adsorbents show unsatisfied adsorption capacity due to diffusion limitation or the lack of enough active surface sites, and some other problems. To improve the adsorbent capability, surface modification of nanomaterials with functional polymers is commonly adopted to introduce active adsorption sites and reduce their aggregation.[26-30] Some previous reports have demonstrated that these nanomaterials based nanocomposites could show obviously improved adsorption capability as compared with unmodified ones.[22, 23]

CNT are one of the most popular one-dimensional carbon nanomaterials, which have attracted broad research interest from all over the world because of their unique structure and excellent physical, chemical, electrical, thermal and mechanical properties.[31] Despite much progress has been made in the environmental applications of CNT, practical utilization of unmodified CNT for adsorption application is

severely hindered by their agglomeration. It is well known that pristine CNT tended to agglomerate into large clusters for their large specific surface area and strong hydrophobic interaction between the individual CNT. Apart from the aggregation of CNT that will lead to the decrease of the specific surface area, the pristine CNT are mainly composed with hydrophobic carbon atoms and lack of functional groups.[31, 32] Therefore surface modification of CNT to introduce adsorption active sites is required to improve their adsorption capability. Although a number of methods have reported for the surface modification of CNT, most of them are rather complex, low efficient and high cost. Therefore, novel, simple and effective surface modification strategies are still highly desirable to extend and improve the performance of CNT in environmental applications. Chitosan is the alkaline deacetylated product of chitin. It is widely applied in water treatment because of its special characteristic such as non-toxicity, biocompatibility, biodegradability, low cost, abundant in nature and desirable adsorption capability.[33-36] Because chitosan possesses abundant amino, carboxyl and hydroxyl functional groups which can serve as coordination sites and exhibit a high specificity towards heavy metal ions.[37, 38] However, the application of chitosan is hindered by its less density, settling slowly and dissolves in dilute acidic solution. Therefore the immobilization of chitosan on CNT to form CNT based chitosan nanocomposites is expected to overcome the disadvantages both of CNT and chitosan.

In this contribution, we present a novel and facile method to create the CNT-PDA-CS nano-adsorbents through the combination of mussel-inspired chemistry and Michael addition reaction. The experimental procedure for preparation of CNT-PDA-CS nanocomposites is displayed in **Scheme 1**. First, CNT were coated with polydopamine (PDA) thin films via self polymerization of dopamine under alkaline Tris (hydroxymethyl) aminomethane (Tris) solution. Secondly, the carboxymethyl chitosan was subsequently attached onto CNT-PDA through Michael addition reaction between the PDA thin films and the amino groups of carboxymethyl chitosan. The successful preparation of the resultant adsorbents (CNT-PDA-CS) was evidenced by a number of characterization techniques. Furthermore, the adsorption application of

CNT-PDA-CS for Cu^{2+} removal was examined. Because of the existence of functional groups such as carboxyl groups, amino groups and hydroxyl groups on the surface of CNT based nanocomposites, the CNT-PDA-CS exhibited obviously enhanced adsorption capability towards copper ions as compared with the unmodified CNT. Taken together, we have developed a novel, simple and universal strategy to prepare CNT based nano-adsorbents with high efficiency for removal of heavy metal ions from aqueous solution. These mussel inspired strategy should be a general method to fabricate various nanocomposites for environmental applications because of the universal and strong adhesion of PDA towards almost any materials and surface.[39, 40]

Scheme 1 the preparation of CNT-PDA-CS nanocomposites via a combination of mussel-inspired chemistry and a Michael addition reaction.

Experiment

2.1. Materials and characterization

Dopamine hydrochloride was purchased from Sangon Biotech. Co., Ltd (Shanghai, China). CNT (> 95%, diameter of 30 to 50 nm) were purchased from Sino Nanotech Ltd. (Beijing, China). Tris (hydroxymethyl) aminomethane (Tris) and carboxylated chitosan are obtained from Aladdin Company (Shanghai China). All the other reagents are of analytical grade and used without further purification. Solution pH was monitored with a pH meter (Mettler-Toledo International Inc., China), fitted with a combined glass electrode (0.01 pH

units). Transmission electron microscopy (TEM) images were recorded on a Hitachi 7650B microscope operated at 80 kV using a carbon-coated copper grid. The Fourier transform infrared (FT-IR) spectra were obtained by using a Nicolet 380 Fourier transform spectrometer. The samples were pressed with KBr into a pellet before measuring the infrared absorption spectra. Thermal gravimetric analysis (TGA) was conducted on a TA instrument Q50 with a heating rate of 20 °C min⁻¹ under protection with N₂. The X-ray photoelectron spectra (XPS) were performed on a VGESCALAB 220-IXL spectrometer using an Al K α X-ray source (1486.6 eV). The energy scale was internally calibrated by referencing to the binding energy (E_b) of the C1s peak of a carbon contaminant at 284.6 eV.

2.2. Preparation of CNT-PDA

Dopamine solution with 5 g/L were prepared by dissolving dopamine in Tris buffer solution (10 mM, pH = 8.5). Then 500 mg of CNT were suspended in the 100 mL of dopamine solution under stirring for 6 h. After polymerization, the CNT coated with polydopamine (PDA) were separated by centrifugation at 8000 rpm for 10 min (Shuke Centrifuge TG-16, Sichuan shuke instrument Co., Ltd., China) and washed with deionized water several times. Finally, the precipitations were dried in the oven at 60 °C for 12 h. These as-synthesized CNT-PDA nanocomposites were collected and stored in vials for further characterization and experiments.

2.4. Preparation of CNT-PDA-CS

200 mg of CNT-PDA was dispersed in Tris buffer solution (10 mM, pH = 8.5). 200 mg of chitosan was then added into the solution and stirred for 6 h at room temperature. These as-synthesized CNT-PDA-CS nanocomposites were collected and stored in vials for further characterization and experiments.

2.5. Adsorption experiments

The adsorption of Cu²⁺ on CNT-PDA-CS nanocomposites was investigate by a batch adsorption experiments and the effects of different conditions such as contact time, pH value, temperature, and the initial Cu²⁺ concentration were explored. The adsorption experiments were carried out in the 50 mL

polyethylene tubes. 10 mg adsorbents were added into 50 mL of 4 mg L⁻¹ Cu²⁺ solution. The equilibrium Cu²⁺ concentrations were determined using the UV-Vis spectrophotometer at 774 nm. The same procedure was used for investigating the effect of contact temperature (295, 305, 315, 325, 335 and 345 K), pH values from 3 to 10 by adding 0.1 M HCl or 0.1 M NaOH solutions and initial Cu²⁺ concentrations ranging from 4 to 80 mg/L. The equilibrium amount of adsorption (Q_e) and the amount of adsorption (Q_t) was analyzed based on the following equations:

$$Q_e = \frac{C_0 - C_e}{W} \times V$$

$$Q_t = \frac{C_0 - C_t}{W} \times V$$

Where V (mL) is the volume of the solution, W (g) is the dry weight of CNT-PDA-CS adsorbent, C_0 (mg L⁻¹), C_e (mg L⁻¹) and C_t (mg L⁻¹) are Cu²⁺ concentrations at the initial, equilibrium time and time t (min).

3 Results and discussion

3.1 Characterization of CNT samples

Fig. 1 shows the TEM images of pristine CNT (A), CNT-PDA (B) and CNT-PDA-CS (C). It can be clearly seen the CNT in the **Fig. 1A**, and the diameter of CNT were between 30 and 50 nm. After modification with PDA and chitosan, the morphology of CNT has not obviously changed. However, some thin films coated on the CNT surfaces can be clearly identified by TEM images from **Fig. 1B** and **Fig. 1C**. The emergence of polymer thin films provided direct information about the successful coating of CNT by PDA and chitosan through the combination of mussel inspired chemistry and Michael addition reaction. The coating of CNT with PDA is mainly based on the strong adhesion of PDA towards various materials and surfaces. However, the linkage of chitosan on PDA functionalized CNT is possibly relied on the Michael addition reaction between the amino groups of chitosan and PDA. As compared other surface modification strategies, the method described in this work shows some advantages. For example, the self polymerization of dopamine and subsequently Michael addition reaction can be occurred under rather mild reaction conditions such as room temperature, aqueous solution, air atmosphere and absent of catalysts. More

importantly, these reactions are not involved hazardous reagents and thus can preserve the structure and morphology of CNT very well. Furthermore, many other commercial available and synthetic polymers can also been immobilized on CNT through the PDA as linkage. Therefore, a large number of multifunctional CNT based polymer nanocomposites can be fabricated, which is of great importance for expand the utilization of CNT.

Fig. 1 TEM images of pristine CNT (A), CNT-PDA (B) and CNT-PDA-CS (C). Scale bar = 200 nm. The emergence of polymer thin films on CNT implied that PDA and chitosan have immobilized on CNT successfully. This is mainly relied on the self polymerization of dopamine and the Michael addition between PDA and amino groups of chitosan.

To obtain further information on the surface composition of the samples, a survey XPS scan ranging from 0 to 1200 eV was carried out for determination of the CNT samples (**Fig. 2**). It can be seen that the elements such as carbon (C), nitrogen (N) and oxygen (O) were observed in the CNT samples (**Fig. 2A**). **Fig. 2B-D** shows the C1s, N1s and O1s XPS spectra of CNT samples. As compared with the pristine CNT, the intensity

of C1s was decreased slightly after their surface was coated with PDA and chitosan. However, it is worth to noting that the intensity of N1s and O1s are significantly increased in the samples of CNT-PDA and CNT-PDA-CS. The C1s of CNT-PDA can be curve-fitted into three peak components with binding energies (BEs) at about 284.6, 285.4 and 286.6 eV, that can be attributed to C-C, C-N and C-O species, respectively (**Fig. S1B**). The C1s of CNT-PDA-CS can be curve-fitted into four peak components with binding energies (BEs) at about 284.6, 285.5, 286.7 and 289.0 eV, attributable to C-C, C-N, C-O and O-C=O species, respectively (**Fig. S1C**). The appearance of the C-N peak component at the BE of 285.5 eV in C1s of CNT-PDA and at the BE of ~400 eV in N1s of CNT-PDA suggested that the CNT has been modified with PDA (**Fig. S1D**). Furthermore, the appearance of the O-C=O peak component at the BE of 289.0 eV in C1s of CNT-PDA-CS is consistent with the presence of -COOH group in the chitosan. All of the above results clearly confirmed that CNT have been functionalized with PDA and chitosan via combination of mussel inspired chemistry and Michael addition reaction.

Fig. 2 XPS spectra of CNT samples. (A) Survey scan curves range from 0 to 1200 eV, (B) The C1s region, (C) N1s region and (D) O1s region. The obvious increase of intensity of N1s and O1s clearly demonstrated

the coating of CNT by PDA and chitosan.

The element contents (C, N, O) of CNT samples are listed in **Table 1**. From **Table 1**, the C1s content decreases from 97.13% of pure CNT to 80.12% of CNT-PDA, while the O1s percentage increases from 2.87% to 12.08%, and a new element N was found in the sample of CNT-PDA. The emergence of element N and obvious increase of the intensity of O1s clearly demonstrated that PDA were successfully coated on the CNT through self polymerization of dopamine. After further modification of CNT-PDA with chitosan, the element percentages of C and N were changed from 84.00% and 12.08% to 86.14% and 2.37%, respectively. These results further indicate that CNT-PDA can be successfully functionalized chitosan through the Michael addition reaction between PDA and amino groups of chitosan. Due to the existence of many types of functional groups on PDA and chitosan, the resultant CNT-PDA-CS nanocomposites are expected to displayed higher adsorption capability as compared with the pristine CNT.

Table 1 Element contents (%) of CNT samples based on XPS analysis

Samples	C1s	O1s	N1s
CNT	97.13	2.87	0
CNT-PDA	84.00	12.08	3.92
CNT-PDA-CS	86.14	11.49	2.37

Fig. 3 displays the FT-IR spectra for CNT, CNT-PDA and CNT-PDA-CS. No specific adsorption peaks were observed in the sample of pristine CNT. However, the broad band at 3431 cm^{-1} that attributed to the inter- and intra- molecular hydrogen bonding of both $-\text{NH}_2$ and $-\text{OH}$ stretching vibration was obviously enhanced in the sample of CNT-PDA (**Fig. 3**). This indicated the successful modification of CNT by PDA through mussel inspired chemistry. After further surface modification with chitosan, the relative intensity of

the absorbance bands at around 1634 cm^{-1} was obviously enhanced. The emerged signal at 1634 cm^{-1} should be assigned to C=O of N-acetyl groups of chitosan. On the other hand, two peaks at 1406 and 1094 cm^{-1} ascribed to C-H bending vibration and C-O stretching vibration mode were also found in the sample of CNT-PDA-CS. The difference between the FT-IR spectra of CNT-PDA and CNT-PDA-CS further confirmed that chitosan has linked on CNT-PDA through Michael addition reaction.

Fig. 3 FT-IR spectra of CNT samples. As compared with pristine CNT, a series of peaks at 3431 , 1634 , 1406 and 1094 cm^{-1} were found in the sample of CNT-PDA-CS. These characteristic peaks indicated that the functional groups such as amino, hydroxyl and carboxyl groups were presented in the sample of CNT-PDA-CS.

The successful modification of CNT with chitosan through mussel inspired chemistry and Michael addition reaction was further confirmed by TGA. As shown in **Fig. 4**, the weight loss percentage of pristine CNT was 2.75% when the temperature was up to $600\text{ }^{\circ}\text{C}$. This result implied that pristine CNT possess high purity, good thermal stability and lack of functional groups. However, after modification with PDA and chitosan, the weight loss of CNT-PDA and CNT-PDA-CS was significantly increased to 25.41% and 31.89% ,

respectively. Based on the TGA results, the mass percentages of polymer conjugated on the surface of CNT were calculated to be 22.66% and 29.14% for CNT-PDA and CNT-PDA-CS, respectively. The significant difference in the thermal stability of pristine CNT and modified CNT samples clearly demonstrated that PDA and chitosan are indeed coated on the surface of CNT utilizing the strategy described in this work.

Fig. 4 TGA curves of CNT, CNT-PDA and CNT-PDA-CS. It can be seen that the weight loss of modified CNT samples was significantly increased as compared with the pristine CNT. These results indicated that PDA and chitosan have successfully coated on CNT through self polymerization of dopamine and Michael addition reaction.

3.2 Adsorption experiment studies

3.2.1 Effect of contact time and adsorption kinetics

Fig. 5 shows the relationship of contact time and the adsorption capacity of Cu^{2+} onto CNT samples. It can be seen that the adsorption equilibrium time of CNT and CNT-PDA-CS is about 40-50 min. As

compared with the pristine CNT, CNT-PDA-CS shows much higher adsorption capability at the same adsorption conditions. This could be attributed to the introduction of -NH_2 and -COOH on the surface of CNT through formation of PDA thin films and subsequent conjugation with chitosan (**Fig. 5A**). On the other hand, the adsorption kinetics of CNT-PDA-CS was fitted by pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The adsorption capability of CNT-PDA-CS was 31.70 and 38.18 mg g^{-1} based on pseudo-first-order, pseudo-second-order models, respectively.

Fig. 5 (A) Effect of contact time on Cu^{2+} removal by CNT and CNT-PDA-CS, (B) The adsorption kinetics of CNT-PDA-CS fitted by pseudo-first-order, pseudo-second-order and intraparticle diffusion models. (The initial Cu^{2+} concentration was 4 mg L^{-1} , $\text{pH} = 7.0$ and $T = 303 \text{ K}$)

The non-linear form of the pseudo-first-order kinetic model can be expressed as follows:

$$Q_t = Q_e (1 - e^{-k_1 t})$$

Where Q_e (mg g^{-1}) is the adsorption capacity at equilibrium and Q_t (mg g^{-1}) is the amount of Cu^{2+} adsorbed by CNT-PDA-CS at time t (min), k_1 (min^{-1}) is the rate constant of the pseudo-first-order equation and the relevant data are calculated and listed in **Table 2**.

Table 2 Data of pseudo-first-order, pseudo-second-order and intraparticle diffusion models parameters at 303 K.

Models	Parameters	Initial concentration (mg L ⁻¹)
		4
Pseudo-first-order equation	$Q_e(cal)$ (mg g ⁻¹)	31.70
	k_1 (min ⁻¹)	0.1259
	R^2	0.9844
Pseudo-second-order equation	$Q_e(cal)$ (mg g ⁻¹)	38.18
	k_2 (g mg ⁻¹ min ⁻¹)	0.0038
	h (mg g ⁻¹ min ⁻¹)	5.464
	R^2	0.9917
Intraparticle diffusion	k_p (mg g ⁻¹ min ^{-0.5})	2.988
	R^2	0.8737

The non-linear form of pseudo-second-order kinetic model is given as:

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t}$$

$$h = k_2 Q_e^2$$

Where Q_e (mg g⁻¹) and Q_t (mg g⁻¹) are the adsorption capacity of CNT-PDA-CS at equilibrium and any time t (min), k_2 (g mg⁻¹ min⁻¹) is the pseudo-second-order rate constant and h (mg g⁻¹ min) represents the initial adsorption rate. All the parameters are shown in **Table 2**. As we can see, the value of correlation coefficient (R^2) of the pseudo-second-order model (0.9917) is higher than that of the pseudo-first-order

kinetic model (0.9844), which indicated that the experimental data for the adsorption of Cu^{2+} ions onto CNT-PDA-CS in different initial concentrations follows the pseudo-second-order kinetic model better than the pseudo-first-order model. In order to explore and make sure the rate-controlling step of adsorption, the intraparticle diffusion is expressed as:

$$Q_t = k_p t^{0.5}$$

Where k_p ($\text{mg g}^{-1} \text{min}^{-0.5}$) is the rate constant of the intraparticle diffusion. The adsorption process can be divided into three consecutive steps, such as the instantaneous adsorption step, the intraparticle diffusion and the final equilibrium stage. It can be seen that the correlation coefficient of intraparticle diffusion in model is 0.8737, indicating that intraparticle diffusion is the rate-controlled step during the adsorbing process.

3.2.2 Effect of pH values

To investigate the influence of pH values on Cu^{2+} removal, the Cu^{2+} adsorption onto CNT-PDA-CS as a function of pH ranging from 3 to 10 at room temperature is given in **Fig. 6**. The removal of Cu^{2+} by CNT-PDA-CS was highly dependent on pH values. As show in **Fig. 6**, the adsorption capacity of Cu^{2+} was increased from 19 to 36.0 mg/g as the pH was increased from 3 to 10. At low pH values, the adsorption capacity of CNT-PDA-CS was decreased due to the competition for the adsorption sites between H^+ ions and Cu^{2+} in the acidic solution. However, at high pH values, the alkaline environment is beneficial to the formation of coordination from Cu^{2+} and $-\text{NH}_2$ and $-\text{COOH}$ on the surface of CNT-PDA-CS through combination of the impact of porous structure and coordination. Therefore, the CNT-PDA-CS can be regenerated via changing the solution pH values.

Fig. 6 Effect of pH on Cu^{2+} adsorption onto CNT-PDA-CS (the initial concentration of Cu^{2+} is 4 mg/L, $T = 303 \text{ K}$).

3.2.2 Effect of the initial Cu^{2+} concentrations

Freundlich model and Langmuir model are used for fitting the experimental data (**Fig. 7**). The non-linear form of Langmuir model can be expressed by the following equation:

$$Q_e = \frac{bQ_m C_e}{1 + bC_e}$$

Where Q_m (mg g^{-1}) is the maximum amount of the absorbents and b (L mg^{-1}) is the Langmuir adsorption constant related to energy of adsorption, Q_e (mg g^{-1}) is the equilibrium adsorption capacity of CNT-PDA-CS nanocomposites and C_e (mg L^{-1}) is the equilibrium concentration of Cu^{2+} . The parameters of Langmuir and Freundlich model fitting of Cu^{2+} adsorption on CNT-PDA-CS are listed in **Table 3**. In this experiment, the value of Q_m (mg g^{-1}) for CNT-PDA-CS is 112.52 mg g^{-1} at 303 K and the constant b from the Langmuir model is 0.0931 L mg^{-1} .

The Freundlich model can be expressed as:

$$Q_e = K_F C_e^{1/n}$$

Where K_F ($\text{L mg}^{1-n} \text{ g}^{-1}$) is an correlation index reflecting the adsorption capacity and n is the degree of dependence of adsorption at equilibrium concentration. As shown in **Table 3**, the R^2 value of Langmuir

model (0.9736) is higher than the Freundlich model (0.9404), which suggesting that the Langmuir model fits the adsorption data better than Freundlich model.

Fig. 7 The adsorption isotherms of Cu^{2+} by CNT-PDA-CS. (initial concentrations of Cu^{2+} from 4 to 80 mg L^{-1} , adsorbent weight 2 mg, pH = 7.0, t = 60 min, T = 303 K), the data from the experiment have been fitted by Langmuir and Freundlich models.

Table 3 The parameters of Langmuir and Freundlich model fitting of Cu²⁺ adsorption on CNT-PDA-CS.

		Temperature (K)
Isotherms	Parameters	303
Langmuir	Q_0 (mg g ⁻¹)	112.52
	b (L mg ⁻¹)	0.0931
	R^2	0.9736
Freundlich	K_F (L mg ¹⁻ⁿ g ⁻¹)	23.4509
	n	2.9167
	R^2	0.9404

3.2.3 Effect of Temperature and thermodynamic study

The thermodynamics parameters including entropy change (ΔS°), enthalpy change (ΔH°) and Gibbs free energy (ΔG°) can be used to analyze whether the adsorption reaction is endothermic or exothermic, and the values were calculated by the following equations:

$$\ln K_\alpha = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

$$K_\alpha = \frac{C_0 - C_e}{C_e} \frac{V}{m}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Where K_α is the adsorption equilibrium constant, the R is the ideal gas constant (8.314 J mol⁻¹ K⁻¹) and T (K) is the temperature. The enthalpy change (ΔH°) and entropy change (ΔS°) was determined from the slope and intercept of the Van't Hoff plots of $\ln K_\alpha$ versus of $1/T$ (**Fig. 8B**), the relevant data are calculated and listed in **Table 4**. It can be seen that the adsorption of Cu²⁺ was increased with the evaluation of temperature and the value of ΔH° is positive (**Table 4**), which indicated the adsorption process of Cu²⁺ onto

CNT-PDA-CS is endothermic and there are strong interaction between CNT-PDA-CS and Cu^{2+} .

Fig. 8 Effect of temperature on the adsorption of the Cu^{2+} on CNT-PDA-CS (the initial concentration of Cu^{2+} is 4 mg L^{-1} , $\text{pH} = 7.0$, $t = 60 \text{ min}$)

Table 4 Data of the thermodynamic parameters for the adsorption of Cu^{2+} onto CNT-PDA-CS.

T (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ $\text{mol}^{-1} \text{ K}^{-1}$)
295	-3.04	13.77	0.057
305	-3.26	14.13	
315	-4.34	13.62	
325	-5.31	13.22	
335	-5.88	13.21	
345	-6.28	13.38	

3.2.4 Desorption and repeated use

The reusability of CNT-PDA-CS nanocomposites was also investigated in our work, and the desorption experiments were carried out with 0.01 M HNO_3 . As shown in Fig. 9, the adsorption capacity of CNT-PDA-CS was repeated five times, and after each experiment the adsorbent was centrifuged and washed

with 0.01 M HNO_3 . The results suggested that the adsorbent still exhibited good adsorption ability after five cycles of reuse. The slight decrease of adsorption capacity should be attributed to the loss of the adsorbent after washing. Therefore, the CNT-PDA-CS nanocomposites prepared in this work showed a good application prospect as an effective adsorbent for the removal of heavy metal ions from aqueous solution.

Fig. 9 The adsorption capacity of CNT-PDA-CS nanocomposites after five cycles of reuse.

The environmental adsorption application of CNT has attracted great research attention because of their small size and high specific surface areas.[31] A number of environmental pollutants such as dyes, heavy metal ions and radionuclides have been demonstrated by CNT based nanocomposites.[22] However, pristine CNT are lack of functional groups and readily aggregated into large CNT clusters, which will impede the adsorption of environmental pollutants on CNT. Thus many surface modification strategies have been developed to enhance the adsorption capability of CNT.[41-43] For example, Wang et al have demonstrated that CNT can be modified by cyclodextrin and carboxymethyl cellulose using plasma-induced grafting. The resultant CNT based nanocomposites showed enhanced adsorption capability to heavy metal ions.[43] However, these strategies for surface modification of CNT are relative complex, time consuming and requirement of specific and expensive instruments. Therefore, to fabricate high efficient CNT based adsorbents, the development of novel, simple but effective methods for surface modification of CNT is still

of great interest. Mussel inspired chemistry is a recent emerged surface modification method that relied on the strong and universal adhesion of PDA to various materials and surfaces.[40, 44-50] More importantly, the introduction of PDA thin films on the materials and surfaces can endow many secondary reactions on the PDA thin films. For example, the amino and thiol contained compounds can be attached on the PDA thin films coated CNT, graphene oxides as the ad-layers through Michael addition reaction.[26, 27, 51-55] On the other hand, the polymerization initiators could also be immobilized on PDA thin films modified materials that can be used for grafting of polymers through light irradiation initiated polymerization, atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization and single-electron transfer living radical polymerization (SET-LRP).[53, 56-64] In this work, the carboxymethyl chitosan with amino, carboxyl and hydroxyl groups can be facilely conjugated with CNT through the Michael addition reaction between the amino group of CS and PDA thin films, which were coated on CNT via self polymerization of dopamine under weak alkaline solution. As compared with other methods for surface modification of CNT, this method can occur at room temperature in aqueous solution in short term. The resultant CNT-PDA-CS nanocomposites exhibited obviously enhanced adsorption capability towards Cu^{2+} . All of these results confirmed that the mussel inspired chemistry is a very useful strategy for fabrication of high efficient adsorbents for environmental applications.

4. Conclusion

In conclusion, surface modification of CNT with chitosan was achieved via combination of mussel inspired chemistry and Michael addition reaction. A series of characterization techniques were used to ascertain the successful modification of CNT-PDA-CS. The environmental applications of CNT-PDA-CS for removal of Cu^{2+} from aqueous solution were examined. Different experimental conditions such as contact time, pH value, temperature, and the initial Cu^{2+} concentration on the adsorption behavior of CNT-PDA-CS toward Cu^{2+} were investigated in detailed. We demonstrated that the CNT can be facilely and effectively

functionalized with chitosan, which introduced a number of functional groups (e. g. amino group, carboxyl group and hydroxyl group) on CNT. These functional groups on CNT could provide many adsorption active sites for Cu^{2+} , which results in the obviously enhanced adsorption capability of CNT-PDA-CS toward Cu^{2+} . Furthermore, due to the universal of mussel inspired chemistry for surface modification, this strategy could also be used for fabrication of many other highly efficient adsorbents for removal of environmental pollutants. More importantly, many synthetic polymers with different functional groups and properties can also be conjugated on CNT surface through combination of mussel inspired chemistry and different polymerization strategies. Therefore, the mussel inspired chemistry should be a novel, simple and universal route for fabrication of high efficient polymeric nanoadsorbents with promising application prospects.

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High efficient CNT based nanoadsorbents (CNT-PDA-CS) were facilely prepared via combination of mussel inspired chemistry Michael addition reaction and utilized for removal of Cu^{2+} from aqueous solution