

Preparation and Cu (II) Adsorption Characteristics of Carboxymethyl Cross-Linked Sewage Sludge

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Abstract

Sewage sludge was cross-linked with epichlorohydrin to increase its mechanical strength and applicability as an absorbent material. We investigated the effect of the conditions of the cross-linking reaction on the mechanical strength and Cu (II) adsorption capacity of epichlorohydrin cross-linking sewage sludge (ECS). Experimental results showed that cross-linking can raise significantly the mechanical strength of sewage sludge. To improve the adsorption capacity of ECS, carboxymethyl cross-linked sewage sludge (CCS) with maximal adsorption capacity (65mg/g) for Cu (II) was synthesized from ECS by using chloroacetic acid as the etherification agent. The experimental results showed that the adsorption properties of CCS for Cu (II) could best be described by the pseudo-second order model and Langmuir model, and the adsorption mechanism was ion exchange. Our data suggest that CCS is a promising absorbent for removal of heavy metals from wastewater.

Keywords: sewage sludge, cross-linked sewage sludge, carboxymethyl cross-linked sewage sludge, heavy metal adsorption

Introduction

Sewage sludge is residue generated at centralized wastewater treatment plants as a result of the treatment of wastes released from a variety of sources, including homes, industries, medical facilities, street runoff, and businesses. In the past decades, sewage sludge has dramatically increased due to rapid urbanization and has resulted in serious environmental problems. Thus, disposal and resource use of sewage sludge have attracted

much attention [1-4]. Traditional methods for disposing of sewage sludge include application to cropland, landfilling, incineration, and ocean dumping, which have been operated in some countries for many years [5, 6]. The negative environmental effects of these methods have gradually been reflected by the transfer of pollutants from sewage sludge to the soil, the atmosphere, and the ocean. The demand for efficient and environmentally friendly approaches to the utilization of sewage sludge is therefore a matter of urgency. One of these is conversion of sewage sludge into adsorbents.

Many different methods have been proposed and used to convert this waste to a variety of sewage sludge-based adsorbents [6-14], including pyrolysis, chemical

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activation, microwave irradiation, and alkali modification, etc. Because sewage sludge contains carbon and can be made into cheap adsorbents, much research has focused on making use of sewage sludge to prepare carbon-bearing adsorbents for the removal of pollutants from wastewater [10-14]. In fact, sewage sludge is a solid-liquid mixture containing organic fragments, bacteria, inorganic particles, and colloids [15], and has good adsorption performance.

Living bio-sludge acclimatized in synthetic industrial estate wastewater without heavy metals showed the highest Pb (II) and Ni (II) adsorption capacities at 840 and 720 mg/g biosludge, respectively [16]. However, it is difficult for sewage sludge as an adsorbent to be directly used for industrial sites since it tends to break up and disperse in aqueous solutions. Therefore, sewage sludge-based adsorbents with high mechanical strength and adsorption efficiency should be developed, but the related work has not been reported.

The pollution of water resources due to the indiscriminate disposal of heavy metals has been causing worldwide concern for the last few decades. Copper is one of the most important and frequently used metals in industries such as plating, mining, and petroleum refining [8]. These industries produce a great amount of wastewater and sludge containing a high concentration of copper cations, which have negative effects on the water environment. Hence, the removal and recovery of copper from contaminated water and wastewater is important in the protection of the environment and human health.

In this work, sewage sludge was cross-linked with epichlorohydrin to increase its mechanical strength. The effect of the conditions of the cross-linking reaction on the mechanical strength of epichlorohydrin cross-linked sewage sludge (ECS) was investigated. Based on this, carboxymethyl cross-linked sewage sludge (CCS) with high mechanical strength was synthesized from ECS by using chloroacetic acid as the etherification agent. Meanwhile, the adsorption properties of ECS and CCS for Cu (II) were studied. Our data suggest that high-mechanical-strength CCS is a promising adsorbent for removing heavy metals from wastewater.

Materials and Methods

Materials

The solid excess sewage sludge (water content: 70% (w/w)) used in this work came from the Everbright Wastewater Treatment Plant in Jinan, Shandong Province, China. All the reagents used were purchased from Sinopharm Chemical Reagent Co. Ltd.

Preparation of Sewage Sludge Rods

Solid sewage sludge strips about 1 mm in diameter were prepared by the extrusion molding method with syringes, and then the strips were cut into rods about 5 mm long. The resulting sewage sludge rods were dried

for 12 h at 60°C, and then stored in a dryer for later use.

Preparation of Epichlorohydrin Cross-linked Sewage Sludge Rods (ECS)

Five grams of solid sewage sludge rods and an appropriate amount of NaOH were suspended in 50 mL of ethanol with stirring for two hours at room temperature. Then different amounts of epichlorohydrin were added and the mixture was allowed to react for 8 h at different temperatures. The product was subsequently neutralized by washing with an excess of distilled water. Finally, the sample was dried for 12 h at 60°C and stored in a dryer for the determination of its adsorption and mechanical properties.

Preparation of Carboxymethyl Cross-linked Sewage Sludge Rods (CCS)

Carboxymethyl cross-linked sewage sludge was prepared by a modified Kim and Lim's method [17]. 5 g of ECS and 5 g of NaOH were suspended in 50 ml of ethanol with stirring for two hours at room temperature. 5 g of chloroacetic acid was added and the mixture was allowed to react for 6 h at 80°C. After the reaction, the product was subsequently neutralized by washing with an excess of distilled water, and then dried for 12 h at 60°C. Finally the sample was stored in a dryer for the determination of its adsorption and mechanical properties.

Adsorption Experiments of ECS and CCS

An aqueous solution of copper ions was prepared by dissolving cupric sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in distilled water. ECS or CCS (about 0.2 g) was added to 100 mg/L of Cu (II) copper sulfate solution (200 ml, pH 5), and the mixture was shaken on a rotating shaker for 72 h at 150 rpm at 30°C. The concentration of Cu (II) remaining in the supernatant was determined by means of spectrophotometry using the Cu (II) dicyclohexanoneoxaly dihydrazone colour system (Shimadzu UV-3100 spectrophotometer with 600 nm) [18]. The amount of Cu (II) adsorbed on ECS or CCS, Q_e (mg/g dry weight), was calculated from the mass balance equation:

$$Q_e = (C_0 - C_e) V/m$$

...where C_0 and C_e are the concentrations of Cu (II) at initial and measuring time in the solution, V is the volume of the aqueous solution, and m (g) is the weight of the ECS or CCS.

Evaluation of Mechanical Strength of ECS and CCS

Referencing the measuring method of friability of powder material [19], the mechanical strength of ECS and CCS was evaluated by their loss-weight rate (LWR) in the

shaking process. ECS or CCS (about 1.0 g, W_1) was added to 100 ml of distilled water in a 250 ml reagent bottle and the mixture was shaken on a rotating shaker for 72 h at 200 rpm at 30°C. Then the samples above 20 mesh (pore diameter 800 μ m) were collected, dried for 12h at 60°C, and weighed (W_2) again. LWR was calculated from the equation:

$$LWR = (W_1 - W_2) / W_1 \times 100\%$$

Effect of pH on Adsorption of Cu (II) on CCS

The effect of pH on the adsorption amount of Cu (II) on CCS was studied at pH values ranging from two to five (adjusted with HCl) using a process similar to the already-described adsorption experiments.

Infrared Spectroscopy

Infrared spectra were recorded in KBr discs on a Nicolet AVATAR370 FTIR spectrometer under dry air at room temperature. An appropriate amount of the dried sewage sludge or ECS or CCS was blended with KBr (IR grade) and some of the mixture was pelleted for IR spectral measurement.

Results and Discussion

Effect of Amount of Added Epichlorohydrin on Qe and LWR of ECS

In the procedure of synthesis of ECS (method: preparation of epichlorohydrin cross-linking sewage sludge rods), the amount of added NaOH was 5 g, and the temperature for reaction was 60°C. The influence of the amount of added epichlorohydrin on Qe and LWR of ECS is shown in Table 1. It can be seen that the LWR of ECS rapidly decreases with increasing amounts of added epichlorohydrin over the range 0-25 ml, suggesting that the mechanical property is improved in this process. However, change of the mechanical strength was not obvious when the amount of epichlorohydrin was above 25 ml. It can also be seen from Table 1 that the adsorption ability of ECS changes very little when increasing the amount of added epichlorohydrin over the range 10-30 ml. This result indicates that the cross-linking reaction of epichlorohydrin with sewage sludge has little influence on

Table 1. Effect of amount of added epichlorohydrin on Qe and LWR of ECS.

No.	1	2	3	4	5
Epichlorohydrin(ml)	0	10	20	25	30
Qe (mg /g)	51	34	34	35	36
LWR	98	42	15	7.8	7.3

Table 2. Effect of amount of added NaOH on Qe and LWR of ECS.

No.	1	2	3	4	5
NaOH (g)	0	2	4	6	8
Qe (mg/g)	27	32	35	35	36
LWR	67	45	19	7.5	8.0

the density of the adsorption sites of Cu (II) on sewage sludge. It is noteworthy that the amount of Cu (II) adsorption on the ECS (No. 1 in Table 1) (51mg/g) was obviously more than other samples when the amount of added epichlorohydrin was zero. There are two possible reasons for this phenomenon. First, the NaOH-treated sewage sludge easily disperses during the adsorption experiments because of the lack of the cross-linked structure of epichlorohydrin and possessing high surface areas. Second, NaOH reacts with some sewage sludge constitutions, such as amides and esters, to form new functional groups with the adsorption ability for Cu (II).

As the above results showed, ECS possesses better mechanical properties and adsorption ability when the amount of added epichlorohydrin is 25 ml. Based on this, the effect of NaOH on Qe and the mechanical property of ECS were further investigated.

Effect of Amount of Added NaOH on Qe and LWR of ECS

Table 2 shows the effect of the amount of added NaOH on Qe and LWR of ECS. The preparation conditions of these samples were the same as those of the above section except that the amount of added epichlorohydrin was 25 ml. It can be seen from Table 2 that ECS has good mechanical properties when the amount of NaOH is more than 4 g. The results of Table 2 also show that Qe has a slowly increasing tendency with an increasing amount of NaOH. The probable reason for this, revealed by the above section, is that NaOH reacts with some sewage sludge constitutions to form some new functional groups with the adsorption ability for Cu (II).

Effect of Temperature on Qe and LWR of ECS

At the optimal amount of added NaOH (5g) and epichlorohydrin (25 ml), the influence of the temperature on Qe and LWR of ECS is shown in Table 3. The results show that ECS has good mechanical properties when the

Table 3. Effect of temperature on Qe and LWR of ECS.

No.	1	2	3	4
Temperature (°C)	20	40	60	80
Qe (mg/g)	38	39	35	35
LWR	56	43	7.5	9.0

reaction temperature is higher than 60°C. However, the effect of the temperature in the range of 20-80°C on Q_e was insignificant.

According to the above experimental results, the optimum synthetic conditions for ECS with good adsorption ability and mechanical properties are as follows: the reaction temperature is 60°C and the amount of the added epichlorohydrin and NaOH are 25 ml and 5 g, respectively. The resulting sample (ECS No. 3 in Table 3) was named ECSi.

Kinetics of Carboxymethyl Cross-linked Sewage Sludge

Usually, metal binding to sewage sludge occurs via ion exchange as well as by electrostatic interaction, and the major binding sites are the carboxyl groups [20]. To improve the adsorption capacity of ECSi, carboxymethyl cross-linked sewage sludge (CCS) was synthesized from it. The adsorbed amounts of Cu (II) on the CCS as a function of time at 100 mg Cu (II) / L (200 ml, pH 5) initial concentration are presented in Fig. 1 (a). In addition, the LWR of CCS is 8.7, indicating that it possesses good mechanical properties. To illustrate the validity of carboxymethylation, adsorption kinetics of ECSi for Cu (II) are shown in Fig. 1 (b). It can be seen that the maximum adsorption amount of CCS for Cu (II) is 55 mg/g, noticeably more than that of ECSi (35 mg/g).

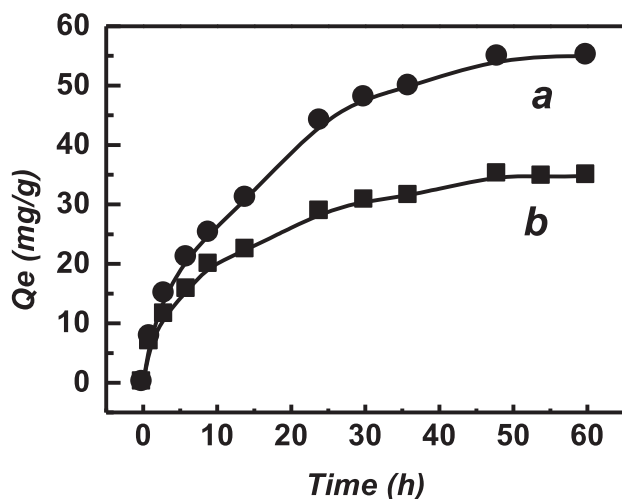


Fig. 1. Adsorbed amounts of Cu (II) on CCS (a) and ECSi (b) as a function of time at 100 mg Cu (II) /L initial concentration (200 ml, pH 5) at 30°C.

However, the adsorption equilibrium of CCS and ECSi are the same amount of time, roughly 50 h.

Several kinetic models are often applied to fit experimental data and to study the mechanisms of the adsorption process. Among them, the pseudo first-order equation, the pseudo second-order equation, and the Weber-Morris method are the most commonly used to describe adsorption kinetics of an adsorbate onto an adsorbent. When the adsorption process is determined by diffusion steps, the kinetics follows the pseudo-first-order rate equation of Lagergren [21-23],

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \quad (1)$$

... where k_1 is the first-order rate constant, Q_e the amount of adsorbate adsorbed at equilibrium, and Q_t the amount of adsorbate adsorbed at time t . The above equation can be transformed into the following formulation utilizing the integration:

$$\log(Q_e - Q_t) = \log Q_e - \left(\frac{k_1}{2.303}\right)t \quad (2)$$

The plot of $\log(Q_e - Q_t)$ vs. t gives a straight line, which allows computation of the adsorption rate constant, k_1 .

The pseudo-second-order equation is given in the following form:

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (3)$$

...where k_2 is the second-order rate constant, and the others are the same as in equation 1.

This model is more likely to predict the kinetic behavior of adsorption with chemical adsorption being the rate-controlling step [22]. Integrating this equation for boundary conditions $t = 0$ ($Q_t = 0$) to t ($Q_t = Q_e$) and then linearizing leads to

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (4)$$

The second-order rate constants k_2 and Q_e are determined from the slope and intercepts of the plot obtained by plotting t/Q_t versus t .

Table 4. Kinetic Parameters for adsorption of Cu (II) ($C_0 = 100$ mg/L) onto the CCS and ECSi.

	Pseudo first order		Pseudo second order		Weber-Morris		
	k_1 (h ⁻¹)	R ²	k_2 (g/(mg.h))	R ²	K_d (mg/(g.h ^{1/2}))	C(mg/g)	R ²
ECSi	0.080	0.97	0.0039	0.99	4.5	3.6	0.96
CCS	0.095	0.88	0.0018	0.99	7.71	1.81	0.98

An intraparticle diffusion model proposed by Weber and Morris is as follows [22]:

$$Q_t = K_d t^{1/2} + C \quad (5)$$

...where K_d is the rate constant of intraparticle diffusion and C is the value of the intercept, which gives an idea about the boundary layer thickness, i.e., the larger the intercept, the greater the boundary layer effect.

The parameters of the linear fitting on t/Q_t vs. t , $\log(Q_e - Q_t)$ vs. t and Q_t vs. $t^{1/2}$ for data of Fig. 1 are given in Table 4. As shown in Table 4, the adsorption of Cu (II) on CCS and ECSi is best described by the pseudo second-order model, indicating that chemical adsorption is the rate-controlling step in the kinetic process.

Adsorption Isotherm of Cu (II) on CCS

The adsorption isotherm Cu (II) on CCS is plotted in Fig. 2 (a). This isotherm describes the equilibrium between the adsorbed Cu (II) concentration (Q_e) in milligrams per gram of CCS (mg/g) and the concentration of Cu (II) remaining in solution (C_e) in mg/L. It is clear that the amount of Cu (II) adsorbed on the CCS linearly increases to 40 mg/g with an increase of the equilibrium concentration of Cu (II) (C_e) to 10 mg/L. When C_e is above 45 mg/L, the increase of Q_e becomes slower. As shown in Fig. 2 (a), the maximal adsorption capacity of CCS for Cu (II) is 65 mg/g. As a comparison, the adsorption isotherm of Cu (II) on ECSi is presented in Fig. 2 (b). The maximal adsorption capacity of the CCS is much larger than that of ECSi (44 mg/g), indicating that carboxymethylation is an effective way to increase the adsorption ability of ECS.

In order to elucidate the adsorption mechanism of the CCS and ECSi for Cu (II), two important isotherms were selected in this study: the Langmuir and the Freundlich isotherm models [21-23]. The Langmuir model is obtained under the ideal assumption of a totally homogeneous adsorption surface and the adsorbate on the adsorbent with the monomolecular layer, whereas the Freundlich isotherm is suitable for a highly heterogeneous surface. The Langmuir model can be expressed by:

$$Q_e = \frac{k_L Q_{\max} C_e}{1 + k_L C_e} \quad (6)$$

...where Q_e is the amount of Cu (II) adsorbed (mg/g), C_e is the equilibrium concentration of Cu (II) (mg/L), and k_L and Q_{\max} are Langmuir constants.

The parameters k_L and Q_{\max} are computed from the linear form of Eq. (6):

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{k_L Q_{\max}} \quad (7)$$

For the Freundlich model, the amount of adsorbate adsorbed, Q_e , is related to the concentration of adsorbate

in the solution C_e through the following equation:

$$Q_e = k_f C_e^{1/n} \quad (8)$$

...where K_f and n are the Freundlich constants. They can be gained from the linear form of Eq. (9):

$$\log Q_e = \frac{1}{n} \log C_e + \log k_f \quad (9)$$

Experimental data in Fig. 2 were fitted to Eq. (7) and Eq. (9). The values of Langmuir constants k_L and Q_{\max} and Freundlich parameters K_f and n are presented in Table 5. The data are better fitted to the Langmuir model than to the Freundlich model. It is inferred that the adsorption surface of CCS and ECSi is closely homogenous. The above results demonstrate that the adsorption characteristics of both CCS and ECSi are essentially similar.

Effect of pH on Q_e of CCS

pH level is one of the most important parameters for the adsorption of Cu (II) from an aqueous solution. To gain further insight into the adsorption process, the effect of pH on Cu (II) adsorption on CCS was studied in the pH range

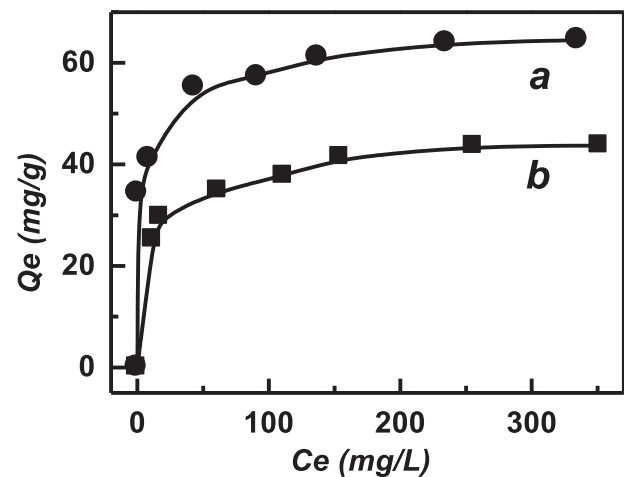


Fig. 2. Adsorption isotherm of Cu (II) onto CCS (a) and ECSi (b) in CuSO_4 solution (pH5) at 30°C.

Table 5. Parameters of Langmuir and Freundlich for adsorption of Cu (II) on CCS and ECSi.

	Langmuir			Freundlich		
	K_L (L/mg)	Q_{\max}	R^2	K_f	n	R^2
ECSi	0.071	45	1.00	17.9	6.3	0.97
CCS	0.15	65	1.00	36	9.70	0.96

Table 6. Effect of pH on adsorption amount of Cu (II) onto CCS.

pH	1	2	3	4	5
Qe (mg/g)	0	0.4	39	44	55

1 to 5. The results are shown in Table 6. The amount of Cu (II) adsorbed on CCS decreases rapidly as pH decreases, and is negligible when pH is below 2. In this case, the degree of ionization of the carboxyls of CCS is so small that it loses the electrostatic binding abilities with Cu (II), implying that the mechanism of the adsorption of Cu (II) to the CCS is ion exchange.

From the above experimental and analytical results, it can be noted that the adsorption capacity of CCS for Cu (II) (65 mg/g) is significantly higher than that of other sewage sludge-derived absorbents, such as sewage sludge carbon (6.7 mg/g) and sewage sludge carbon chemical activation with ZnCl₂ (20.6 mg/g) [24]. The adsorption capacity of CCS is similar to that of commercial cation exchange resins [25, 26], indicating that CCS is a promising absorbent for removal of heavy metals from wastewater.

FTIR

FTIR spectra of dried sewage sludge (a), ECSi (b), and CCS (c) are shown in Fig. 3. In curve a in Fig. 3, the bands at 3,408 cm⁻¹ and 1,654 cm⁻¹ are attributed to the stretching vibration of -OH and -C = O of sewage sludge, respectively. The adsorption band at 2,925 cm⁻¹ could be the asymmetric vibration of -NH. The 1,431 cm⁻¹ is of phenolic -OH and -C-O stretching of carboxylates. The 1,032 cm⁻¹ band could be the vibration of -P-O-C and P-OH of the phosphonate groups [27]. Comparing curve b with curve a in Fig. 3, there is no appreciable difference between the two, suggesting that new infrared active groups have not been formed in ECSi. However, the band at 1,654 cm⁻¹ in curve c broadens, evidently indicating that the density of carboxyl in CCS increases to some extent. This result agrees with its adsorption properties.

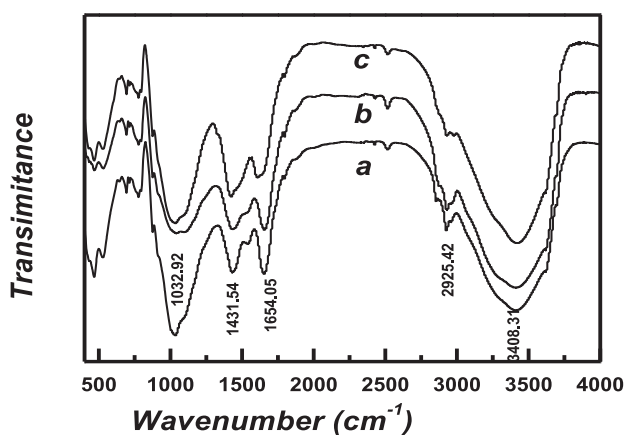


Fig. 3. FTIR spectra of dried sewage sludge (a), ECSi (b), and CCS(c).

Conclusions

Firstly, the synthesized conditions of ECS with good adsorption ability and mechanical strength were studied. The experimental results showed that the optimum conditions were as follows: the amount of the added epichlorohydrin and NaOH to 50 ml of the mixture of dried sewage sludge and ethanol was 25 ml and 5 g, respectively. The reaction temperature was 60°C and the reaction time was 8 h. And then carboxymethylation of ECS was achieved using chloroacetic acid as the etherification. The maximal adsorption capacity of CCS for Cu (II) is 65 mg/g. IR spectrum analysis indicated that the density of carboxyl in CCS increases to some extent compared to ECS.

The experiment results showed that the adsorption properties of CCS for Cu (II) could be best described by the pseudo second-order model and Langmuir model, indicating that chemical adsorption is the rate-controlling step and the adsorption surface is closely homogenous. The mechanism that governs Cu (II) removal by CCS is an ion exchange. Therefore, the use of CCS for the removal of heavy metals from contaminated waters may be a novel and cost-effective alternative.

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