

Effective of Xanthate Modified Chitosan on the Adsorption of Lead Ions

TianguoLi^{1,2}, Tingyu Niu¹, Shaojuan Huang¹, Guangzu Du³*, Bo Li^{1,2}, Fangdong Zhan^{1,2}, Ming Jiang^{1,2}, Yongmei He^{1,2}

¹College of Resources and Environment, Yunnan Agricultural University, Kunming 650201, PR China;

²The Innovation Team for Farmland Non-pollution Production of Yunnan Province, Yunnan Agricultural University, Kunming 650201, PR China

³College of Plant protection, Yunnan Agricultural University, Kunming 650201, PR China;

* Corresponding author: 252653701@qq.com

Abstract. Water lead pollution has a serious threaten to safety of food and ecological. How purify lead polluted wastewater efficiently become an important environmental topic. This study aimed to investigate the effect of the xanthate modified chitosan (XCS) on the adsorption properties of toxic lead from simulated wastewater via static adsorption method. Results showed that the adsorption of lead of both chitosan and XCS depend on solution pH obviously and the optimal pH of 5. The adsorption characteristics of the two adsorbents for lead ions accord with the pseudo-second order kinetics. But the xanthate modify can improve the rate of lead adsorption effectively. Adsorption of lead ions on chitosan follow the Langmuir model, and that of XCS conform to the Freundlich model. However, the effect of temperature on the adsorption capacity was none difference. The lead maximum adsorption capacity of original chitosan and XCS at 40°C was 194.36 mg/g and 317.82 mg/g respectively. The results showed that xanthate modify can improve the adsorption of lead on chitosan and XCS would has great potential for practical application.

1. Introduction

Heavy metals severe contamination in environmental media poses a threat to food and ecological security. Especially, Lead (Pb) is regarded as a hazardous element that has high biotoxicity and carcinogenic. The universal and prominent discharge of Pb accumulated of $7.183 \times 108t$ in the last few decades^[1]. The potential sources of Pb(II) in wastewater include lead mining and metallurgy, electronic manufacturing, pigments, fertilizers and lead-acid batteries^[2]. One of the most medium of Pb exposure, excessive Pb(II) in water is difficult to metabolize, easy to bioaccumulated and magnification which can enter into human body through various ways like breathing, hands, mouth, skin and the food chain. Long-term exposure to Pb(II) can lead to dysfunctions of the system of reproductive, blood and nervous, especially in children^[1-4]. Hence, Lead is classify as a priority issue and the Ministry of Ecology and Environment of the People's Republic of China proposed “zero discharge” for industrial activity, the discharge standards of Pb increasing from 1.0mg/L to 0.01~0.1mg/L which depends on the function of water.

Various physicochemical and biological methods include neutralization, electrochemical, chemical



precipitation, membrane filtration, ion exchange and adsorption have been developed for removal Pb(II) from wastewater to achieve an acceptable concentration of zero discharge [2-5]. The purification technology of Pb(II) in lead waste water from high concentration to dozens of mg/L have been relatively mature and have many industrial applications [6]. Such as chemical precipitation, flocculation electrolysis, electrocoagulation [4-6]. Among these strategies, adsorption techniques have obvious advantages to treat low concentration wastewater. But the removal efficiency was largely impacted by the adsorption performance, chemical stability, cost and regeneration performance of adsorbent [7]. Therefore, the efficient, eco-friendly, and sustainable of adsorbent material is necessary to develop for removal low residual lead wastewater.

Chitosan, a natural biological agent, has excellent metal-binding capabilities due to possessing a high ratio of hydroxyl group (-OH) and amine group (-NH₂) [1, 3, 6-8]. Chitosan has been reported that was an effective adsorbent material for the removal of various organic and inorganic pollutants from aqueous solution [5]. However, the poor stability and insufficient adsorption capacity of chitosan in acidic solutions limit its further application in heavy metal treatment [7-8]. Numerous studies want to improve the adsorption capacity and its stability of chitosan via chemical modification, such as carboxylation, quaternary ammonium salts, sulfhydrylation, phosphates, magnetic and metal salt. According to the HSAB (Hard and soft acids and bases) theory, sulfur group like xanthate and thiol can be classified as soft bases, have a much higher affinity and sorption capacity compared to that of chitosan. Among various sulfur bearing compounds, xanthates are relatively more favorable because of their high insolubility and strong stability with metal ions [9]. To our knowledge, for chitosan, it might oxidize, degenerate, change the structure and modified surface groups in the process of dry heat treatment. However, there have been a few reports on xanthate modification of chitosan through freeze drying treatment after modified synthetically.

In this work, XCS was prepared through a simple process of chitosan xanthation reaction with CS₂ in 5% NaOH aqueous media and then freeze drying treatment. The novel XCS was applicable in removal of Pb²⁺ from wastewater and the adsorption performance and thermodynamic characteristics were investigated and evaluated.

2. Materials and methods

2.1. Chemicals and materials

Chitosan flakes with a deacetylation degree of 90% and CS₂ used in the experiments were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents like NaOH, HNO₃, Pb(NO₃)₂ and anhydrous ethanol used in this work were of analytical pure. Pb²⁺ simulation solution prepared via dissolved Pb(NO₃)₂ in ultrapure water and pH was adjusted by 0.1mol/L NaOH and HNO₃ aqueous solution. Ultrapure water was employed to prepare all the solutions.

2.2. Preparation of XCS

XCS was prepared through chemical grafting of thiol groups with chitosan flakes which carried out according to the process described by Kannamba et al [2, 6, 10]. First, 14% CS₂ (6mL) solution was mixed with 5% NaOH (100mL) solution and pre-reaction was stirred at room temperature for 2h. It was then chitosan flakes (2g) was added to the pre-reaction mixture and stirred at room temperature for 10h. After reaction finished, ethanol (50mL) was mixed to separate precipitates. The precipitate was collected by centrifugation at speed of 3000rpm and washed thoroughly with ultrapure water and anhydrous ethanol alternately until the washer fluid pH was close to neutral. The XCS was obtained when the modified material was freeze-dried for 48h at -50°C. This product served as the adsorbent in further experiments.

2.3. Batch adsorption experiments and analysis

The adsorption property of Pb²⁺ on chitosan and XCS was investigated through batch adsorption studies. The batch experiments were performed by mixing different sorbent with 100mL of Pb(II) simulation solutions into 250mL conical flask. The mixture was placed in a thermostatic oscillator and shaken at a

speed of at 25°C and 150rpm to reach the equilibrium. In the first place, the appropriate initial solution pH (pH=1-5) and dosage of adsorbent (0.01-0.1g/100mL) have been investigated. Except investigate the effects of sorbent dosage, XCS (0.02g) of was taken into each conical flask which contained 100mL of Pb²⁺ solution with initial mass concentration of 10-200 mg/L (for pH, only 100 mg/L was used). The kinetics and isotherm were examined at four kinds of reaction temperature of 25°C, 30°C, 35°C and 40°C. After reaching equilibrium, 10ml supernatants were filtered through a 0.45µm filter membrane and dilute with 1% HNO₃ solution to 100ml for analysis of lead ion concentration.

The Pb²⁺ concentrations were determined by atomic absorption spectrometric method with flame atomization (AAS, TAS-990 AFG). All batch experiments were repeated in triplicate and the average had been reported. The adsorption capacity (q_e (mg/g)) of Pb²⁺ on XCS at equilibrium, and removal rate (w (%)) were calculated to evaluate adsorption efficiency. The kinetic data were analyzed by pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models. The equations are expressed as follows:

$$\text{PFO: } q_t = q_e(1 - e^{(-K_1 t)}) \quad (1)$$

$$\text{PSO: } q_t = \frac{q_e^2 K_2 t}{1 + q_e K_2 t} \quad (2)$$

Where q_e and q_t are represent the adsorption capacity at equilibrium and in time (mg/g), respectively. K_1 (min⁻¹) and K_2 (g/mg.min) are the adsorption rate constants.

To further explore the adsorption behaviors of XCS, classical Langmuir and Freundlich models [12] were employed to analyze the experimental data. They are represented as:

$$\text{Langmuir: } q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3)$$

$$\text{Freundlich: } q_e = K C_e^{1/n} \quad (4)$$

Where q_m is the maximal adsorption capacity (mg/g), b is the Langmuir binding constant, n and K are the adsorption intensity and Freundlich constant, respectively.

3. Results and Discussions

3.1. Effects of initial pH and dosage

Lead distribution and speciation of lead in solution is key condition affecting adsorption performance of Pb²⁺, which main controlled by the acid/alkaline balance. So, the adsorption efficiency of Pb²⁺ on original chitosan and XCS as a function of pH and adsorbent dosage were studied and presented in Fig.1. It can be seen from Fig.1 (a), the removal of Pb²⁺ increases with the increase in pH range from 1 to 5. The highest adsorption were achieved at pH=5 for original chitosan and XCS respectively. And after xanthate modify, the influential effect of initial solution pH on Pb²⁺ adsorption has weakened substantially. There are two possible explanations for the low adsorption at low pH and this difference. First, Pb²⁺ formation of the hydroxyl complexation with the increase of pH and generated precipitates when pH lager than 5. Second large numbers of H⁺ present at low pH protonated the amino (R-NH₂) and xanthate (R-CSSNa) groups on the surface of original chitosan and XCS. Meanwhile, the amino (R-NH₂) and xanthate (R-CSSNa) group is known to be unstable in strong acid solution and to be able to dissociate from the XCS bone [11-14]. R-CSSNa has better insolubility and metal-chelating than the R-NH₂ and made the improvement of Pb²⁺ adsorption efficiency [14]. At the condition of experiments, the removal rate of Pb²⁺ increases from 31.5% to 83.0% for XCS adsorbent, with increasing the dosage from 0.01 to 0.08g/100mL under equilibrium condition.

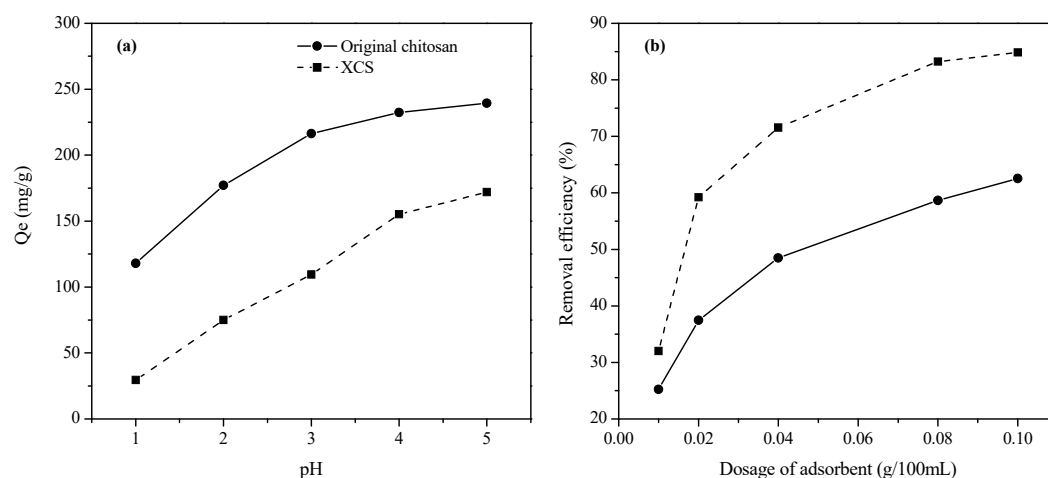


Fig.1 Effect of pH (a) and adsorbent dosage (b) on adsorption of lead on original chitosan and XCS

3.2. Effect of contact time and Adsorption kinetics studies

The adsorption kinetics was investigated for better understanding of the dynamics of adsorption of Pb^{2+} on XCS. Fig.2 illustrates the adsorption of Pb^{2+} on original chitosan and XCS as a function of time at pH 5.

Table 1 Kinetic parameters of adsorbent Pb^{2+} were adsorbed at different initial concentrations

Adsorbent s	Pb^{2+} (mg/L)	Pseudo-first-order			Pseudo-second-order		
		k_1 (min^{-1})	q_e (mg/g)	R^2	K_2 (min^{-1})	q_e (mg/g)	R^2
chitosan	25	0.03	71.06	0.994	2.22	95.08	0.995
	50	0.03	91.02	0.993	2.26	117.68	0.996
	100	0.03	162.32	0.998	1.02	196.90	0.996
	150	0.03	164.10	0.988	1.69	203.10	0.991
	200	0.05	164.14	0.977	2.52	219.10	0.992
XCS	25	0.03	139.02	0.986	1.11	104.02	0.997
	50	0.04	89.37	0.992	1.64	126.37	0.992
	100	0.05	176.87	0.986	9.97	223.87	0.988
	150	0.05	208.34	0.990	8.51	276.34	0.996
	200	0.07	243.67	0.984	8.49	285.74	0.995

It was obvious that the adsorption process proceeds rapidly and the adsorption rate of XCS for Pb^{2+} was significantly faster than that for original chitosan. The adsorption equilibrium time is decreased from about 90min to 60min after xanthate modify. Pseudo-first-order and pseudo-second-order kinetics models were applied to model the adsorption of Pb^{2+} on XCS adsorbent (Fig.2). The kinetic parameters estimated by the three models are presented in Table 1. Obviously, the adsorption process could be well described by the pseudo-second-order equation, indicating the process mechanism to be chemical adsorption of both adsorbents. These indicate that Pb^{2+} could be bound to XCS through the exchange of protons on $R\text{-CSSNa}/R\text{-CSSH}_2^+$ groups and complexation interaction with xanthate [4, 13].

3.3. Adsorption isotherm studies

Isotherm study was performed to obtain the maximum uptake of each lead and for Pb^{2+} concentrations ranging from 10 to 200mg/L at 25-40°C. The Langmuir and Freundlich isotherms were employed to provide insight into Pb^{2+} mode of adsorption by XCS adsorbent. The adsorption isotherms of Pb^{2+} onto

original chitosan and XCS adsorbents displayed in Fig.3 and equilibrium constants provided in Table 2.

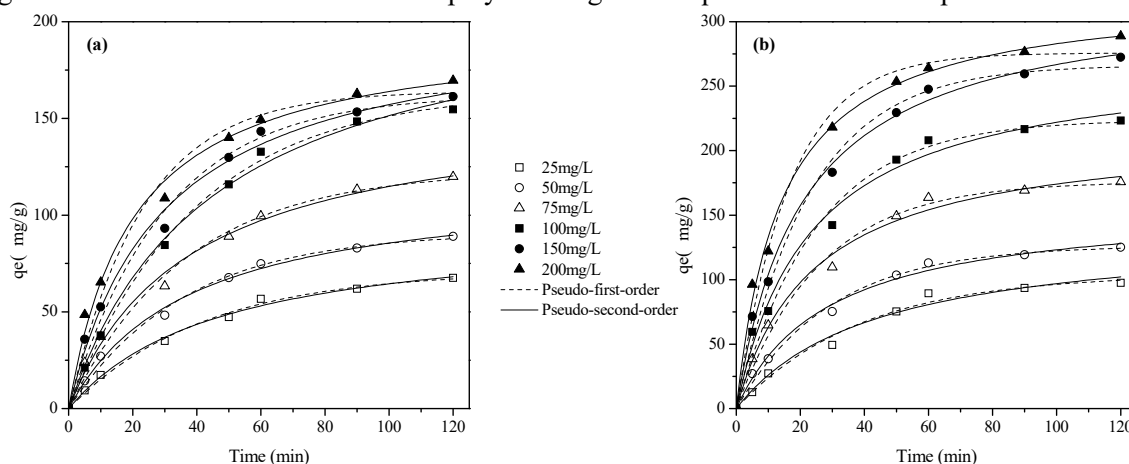


Fig.2 Pseudo-first-order (a) and Pseudo-second-order (b) adsorption kinetics model for Pb^{2+} sorption onto original chitosan (a) and XCS (b) adsorbent (Experiment conditions: $\text{pH} = 5 \pm 0.2$, adsorbent dosage = 0.02 g/100mL, $T = 25 \pm 1^\circ\text{C}$)

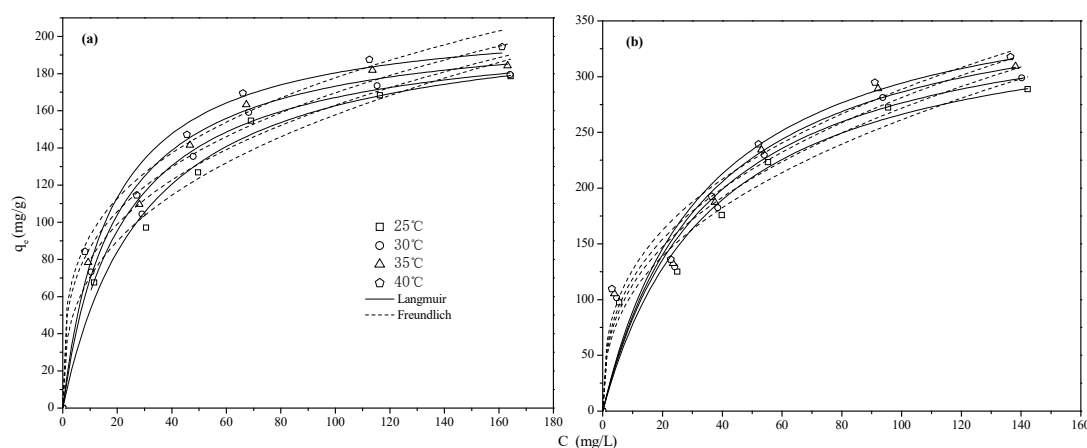


Fig.3 Isothermal fitting for Pb^{2+} sorption onto original chitosan (a) and XCS (b) adsorbents (Experiment conditions: $\text{pH} = 5 \pm 0.2$, adsorbent dosage = 0.02 g/100mL, $T = 25\text{-}40 \pm 1^\circ\text{C}$)

Pb^{2+} uptakes followed the usual adsorption phenomenon where sorption efficiency comparatively decreases with increasing initial Pb^{2+} content [9, 15]. High values of correlation coefficient (R^2) indicate that both the Langmuir (≥ 0.91) and Freundlich (≥ 0.93) equations provide an accurate description of the experimental data as both monolayer adsorption and heterogeneous surface conditions exist under the adsorption situations [12]. And compared with original chitosan, Freundlich isotherm provided more accurate alignment with the experimental data than the Langmuir model for Pb^{2+} adsorption on XCS depicted the changing of heterogeneous surface and the predominant mechanism was multilayer adsorption. The Langmuir model predicted highest uptake onto XCS of 394.78 mg/g is higher than original chitosan of 212.08 mg/g at 40°C . This prediction pattern was consistent with that observed in some other studies and indicated that xanthate modify can improve the metal adsorption capacity of chitosan through Enhanced chelation effect [13-14]. The maximum adsorption capacity increased with the increasing of temperature indicating the endothermic nature of the Pb^{2+} adsorption reaction.

Table 2 The thermodynamic parameters of adsorbent Pb^{2+} were adsorbed at different reaction temperature

Adsorbent s	Temp. (°C)	Langmuir			Freundlich		
		$Q_{\max}$ (mg/g)	b (L/mg)	R^2	K	1/n	R^2
chitosan	25	205.72	0.04	0.98	31.48	0.35	0.98
	30	207.74	0.05	0.98	39.06	0.31	0.93
	35	211.73	0.06	0.99	43.92	0.29	0.98
	40	212.08	0.03	0.98	48.38	0.28	0.98
XCS	25	364.32	0.03	0.94	38.07	0.42	0.97
	30	373.22	0.03	0.93	42.97	0.39	0.97
	35	386.89	0.03	0.91	50.21	0.37	0.97
	40	394.78	0.03	0.90	55.53	0.36	0.96

4. Conclusions

XCS was obtained from two steps chemically modified procedure and freeze drying treatment successfully synthesized in the study. Result shown that xanthate-modified can enhancing Pb^{2+} removal in wastewater and overcome the deficiencies of low Pb^{2+} uptake and high solubility in acid conditions of chitosan. The Pb^{2+} adsorption behaviour of both original chitosan and XCS were affected by solution pH obviously. Pb^{2+} adsorption kinetic of XCS was best described by a pseudo-second-order kinetic model and Freundlich isotherm, and the predominant mechanism was Pb^{2+} complexation with xanthate and expressed multilayer adsorption. Compared with original chitosan, XCS possessed a good ability for Pb^{2+} removal and the maximum adsorption capacity of lead improved from 194.36mg/g to 317.82mg/g. xanthate-modified can improve the metal ions adsorption efficiency of chitosan and has a greatly applied potentiality.

Acknowledgement

This work was supported by the Natural Science Foundation of China (41701362), Yunnan Applied Basic Research Projects (2018FD020) and Innovation Team for Farmland Non-pollution Production of Yunnan Province (2017HC015).

References

- [1] Wang N, Xu X, Li H, et al 2016 *Industrial & Engineering Chemistry Research* **55** 960
- [2] Chang Q, Hao X, Duan L 2008 *Journal of Hazardous Materials* **159** 548
- [3] Duan J C, Qi L, Chen R W, et al 2010 *Carbohydrate Polymers* **80** 436
- [4] Bediako J K, Wei W, Kim S, et al 2015 *Journal of Hazardous Materials* **299** 550
- [5] Kannamba B, Reddy K L, Apparao B V 2010 *Journal of Hazardous Materials* **175** 939
- [6] Ilaiyaraja P, Deb A K S, Ponraju D, et al 2014 *Desalination & Water Treatment* **52** 438
- [7] Wang N, Xu X, Li H, et al 2016 *Industrial & Engineering Chemistry Research* **55** 47
- [8] Zheng L, Meng P 2016 *Journal of the Taiwan Institute of Chemical Engineers* **58** 391
- [9] Chen Y W, Wang J L 2012 *Nuclear Engineering and Design* **242** 452
- [10] Singha A S, Guleria A 2015 *Engineering in Agriculture Environment & Food* **8** 52
- [11] Chen Y, Wang J 2012 *Nuclear Engineering & Design* **242** 452
- [12] Liang S, Guo X Y, Feng N C 2009 *Journal of Hazardous Materials* **170** 425
- [13] Zhu Y, Hu J, Wang J 2012 *Journal of Hazardous Materials* **221** 155
- [14] Pillai S S, Deepa B, Abraham E, et al 2013 *Ecotoxicology & Environmental Safety* **98** 352
- [15] Liang S, Guo X, Feng N, et al 2009 *Journal of Hazardous Materials* **170** 425