

Bio-Sorbents from Cassava Waste Biomass and Its Performance in Removal of Pb^{2+} from Aqueous Solution

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ABSTRACT: Cassava xanthogenate and their derivatives, as adsorbents to remove Pb^{2+} from aqueous solution, are studied based upon orthogonal factorial design. The structural and thermal properties, adsorption performance as well as equilibrium-kinetics are comprehensively investigated with multiple tools, such as Fourier transform infrared spectroscopy, thermal gravimetric analysis (TGA), and UV-visible spectrum technique. The influence of multiple parameters, including initial Pb^{2+} concentrations, compositions, pH values, and temperatures, on the adsorption performance is emphasized. The crosslinked cassava xanthogenate serves as an effective bio-sorbent to remove Pb ions from aqueous solution, allowing regeneration in dilute acid solution. The findings in this study are beneficial for the development of adsorbents from cassava waste biomass and may contribute to environment recovery in “nature-to-nature” manner. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39780.

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INTRODUCTION

Heavy metals, as one set of contamination resource of waste water, have become a major threat to environment due to their bio-accumulation tendency and toxicity in plant, animal, and human lives.^{1–3} The heavy metals, obtaining wide utility in various industries, such as battery manufacture, printing, photographic materials production, etc., cause adverse health effects as their presence in drinking water are above certain threshold values.⁴ Thus, the development of adsorbing technology to remove the heavy metals from industrial wastewater is of great scientific and practical significance. In recent years, great efforts have been made to exploit original or modified agricultural waste biomass, i.e., thioglycolic acid modified cassava waste biomass, as adsorbents for removal of trace amounts of toxic metal ions from industrial waste water.^{5–7} Low cost, high availability as well as facial production process constitute the primary incentives. For instance, low cost adsorbents derived from agricultural wastes *Rhizopus nigricans* have been demonstrated outstanding capabilities for the removal of Cr (VI),⁷ Cd^{2+} ,⁸ cadmium (II), and zinc (II)⁹ ions from wastewater. Generally speaking, the adsorption performance

of agricultural waste adsorbents is susceptible to multiple factors including compositions, initial ions concentration, pH values, temperature, surface characteristics of the adsorbents.

Cassava, as an important source of starch, constitutes the three major potatoes with potato and sweet potato in the world. Over the past decade, the cultivation and production of cassava have significantly increased in China, particularly in the area of Guangdong, Fujian, and Guangxi provinces. Most of the cassava has been used for producing starch and alcohol while large amount of cassava residue has been left during the production. It is reported that the annual output of the cassava residue is up to 300,000 tons in China.¹⁰ Most of the cassava residue is directly disposed or burned, which cause severely environmental problems. Conversion of these low-value cassava wastes into bio-sorbents which are capable of removing toxic and valuable metals from industrial wastewater would not only dramatically promote the economic interests of cassava industry but also benefit environment remediation.^{11,12}

Recently, intensive research has been carried out on the adsorption of various ions by bio-sorbents, such as removal of Cd

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Table I. Orthogonal Factorial Design of Four Factors and Three Levels for Synthesis of Crosslinked Cassava

Level	Factors			
	Epichlorohydrin/ cassava A (mL/g)	15% KOH solution/ cassava B (mL/g)	Reaction temperature T (°C)	Reaction time t (h)
1	1/15	8/3	35	8
2	4/15	10/3	40	16
3	10/15	12/3	45	24

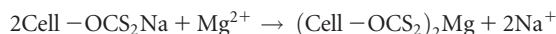
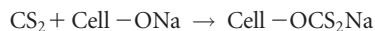
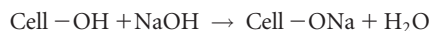
(II), Cu (II), and Zn (II) ions from single-metal ion aqueous solutions by cassava waste biomass¹³ and adsorption of Hg (II), Cu (II), Cd (II), Ni (II) by starch xanthogenate.¹⁴ However, there have been limited amount of reports on the Pb²⁺ adsorption by bio-sorbents so far. Given that the Pb²⁺ is one of the most harmful ions leading to environment contamination, the study on the Pb²⁺ adsorption with low-value bio-adsorbents is of great practical significance. In this study, we reported the work on utility of cassava residual xanthogenate to remove Pb²⁺ from model waste solution by comparison method. The influence of multiple parameters on the ability of ions removal was comprehensively investigated based on orthogonal factorial design. The findings may be helpful for development of novel bio-sorbent from natural resources and offer benefits in rehabilitation of our environment in “nature-to-nature” manner.

EXPERIMENTAL

Preparation of Crosslinked Cassava and Their Xanthogenate

Cassava bagasse came from Guangxi starch Co. (China). After drying at 90°C for 4 days to constant weight, the cassava wastes were ground and sieved through a 100-mesh screen till fine biomass powders were obtained. The crosslinking process was briefly described as follows¹⁵: cassava biomass (15 g) was dispersed into 1% (w/v) sodium chloride solution (150 mL). After adding 5 mL of epichlorohydrin dropwise, 15% (w/v) KOH solution (50 mL) was added into the slurry which was kept at 45°C for 8 h. Subsequently, another 5 mL of epichlorohydrin was added dropwise and reacted for 16 h. Sedimentation, obtained from filtration, was washed by water and ethanol and dried to constant weight in vacuum at the room temperature for 8 h. To confirm the optimized cross-linking conditions effectively, an orthogonal factorial design of four factors in three-level scales, i.e., ratio of epichlorohydrin to cassava, ratio of KOH solution to cassava, reaction temperature and time, was applied. The details are listed in Table I.

Crosslinked cassava (15 g) was put into 20% NaOH solution (200 mL). After agitation for 12 h, carbon disulfide (CS₂, 30 mL), water (100 mL), and 20% NaOH solution (100 mL) were added. The solution was kept at 30°C for 3 h, which was followed by addition of 5% MgSO₄ solution (100 mL). Sedimentation was obtained by filtration. The products were washed by water and ethanol for three times and subsequently dried in vacuum for 12 h. The reaction formulas are illustrated as follows:



The degree of substitution was estimated using a standard volume method for sulfur content (8.42%). Speaking in details, 1 g of crosslinked cassava was put in 100 g distilled water under stirring for overnight. Afterward, the sedimentation volume of the crosslinked cassava was measured. The crosslinking degree was negatively proportional to the sedimentation volume.¹⁵ In order to comprehensively investigate the influence of conditions on composition, an orthogonal factorial design of four factors at three levels, i.e., the ratio of CS₂/cassava, the ratio of 20% NaOH solution/cassava, reaction temperature, and time, was applied in the study, which is shown in Table II.

Characterizations

The structures of cassava, crosslinked cassava, and crosslinked cassava xanthate were measured by a Nexus 670 Fourier Transform Infrared Spectroscopy (FTIR). A model waste water containing lead nitrate in certain concentration was used in adsorption experiments. For the adsorption, pyrolysis, and regeneration measurements, weighted amount of the crosslinked cassava xanthate (0.0275 g, S content equaling 60%) were put into 50 mL lead solution under stirring. The initial ions concentration was 150 mg/L. With the aid of on-line FTIR, adsorption kinetics was evaluated for the solutions in different pH values and at different temperatures. Adsorption capacity was evaluated following the below equation,

$$Q = (C_0 - C_1) \times V / m / 1000 \quad (1)$$

where Q was the adsorption capacity (mg/g), C_0 was the initial concentration (mg/L), C_1 was the residual concentration (mg/L), V was the volume of solution (mL), and m was the weight of adsorbent (g).

RESULTS AND DISCUSSION

Microstructure and Components of Crosslinked Cassava and Their Xanthates

FTIR spectra of cassava, crosslinked cassava, and crosslinked cassava xanthate are shown in Figure 1(a). The adsorption bands of xanthate units typically located in the ranges 1250–1200 cm⁻¹, 1140–1110 cm⁻¹, and 1070–1020 cm⁻¹.¹⁶ However, due to the presence of adsorption disruption deriving from β-(1 → 4)-glycosidic linkages (C–O stretching of C-3 at 1064 cm⁻¹ and of C-6 at 1030 cm⁻¹), the adsorption at 1215 cm⁻¹

Table II. Orthogonal Factorial Design of Four Factors and Three Levels for Synthesis of Crosslinked Cassava Xanthate

Level	Factor			
	CS ₂ /cassava E (mL/g)	20% NaOH solution/cassava F (mL/g)	Reaction temperature G (°C)	Reaction time H (h)
1	2/3	20/3	30	1.5
2	4/3	40/3	35	2.0
3	6/3	60/3	40	3.0

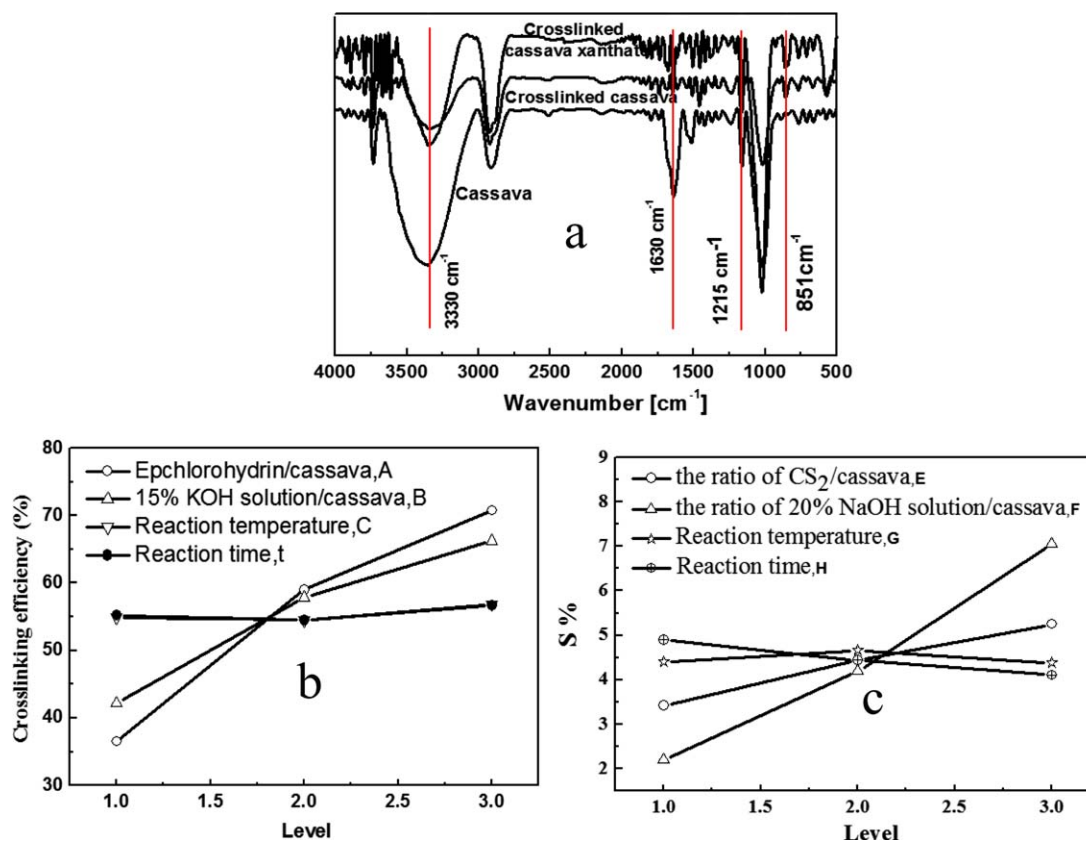


Figure 1. (a) FTIR spectra of cassava, crosslinked cassava, and crosslinked cassava xanthate; (b) plots of crosslinking efficiency against level of the four factors A, B, C, and t ; (c) plots of S content against levels of the four factors E, F, G, and H. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and 760 cm^{-1} were reliably assigned to the stretching and deformation adsorption of the xanthate units, respectively.¹⁷ The appearance of adsorption at 851 cm^{-1} suggested monosubstitution of $\text{CH}_2\text{—OH}$ (C-6) or CH—OH (C-2 or C-3) in the sugar unit of cassava. Besides the bands location, the heights and areas of the adsorption peaks locating at 1630 cm^{-1} and 3330 cm^{-1} varied after the cassava was treated by CS_2 , indicating that the cassava was successfully xanthated. To improve insolubility of the cassava as adsorbents in waste water, the crosslinking of the cassava in this study was improved. The crosslinking efficiency was elaborately investigated as a function of four parameters following orthogonal factorial design, which is shown in the Supporting Information Table S1. The plots of the crosslinking efficiency against factors level are shown in Figure 1(b). The crosslinking efficiency increased with the increase of level for all the four factors. Particularly, the factor A, the ratio of epichlorohydrin/cassava, had the most impact on the variation of the crosslinking efficiency. Similar trend was observed for factor B, i.e., the ratio of alkali solution against cassava, as a result of improving the reaction activity of hydroxyl group. Compared with the factors A and B, the factors C and D had moderate influence on the crosslinking efficiency. The crosslinking efficiency against level of factors E, F, G, and H was measured according to orthogonal factorial design, which is shown in the Supporting Information Table S2. The S content percentages against level for the four factors are plotted in

Figure 1(c). It was found that factor F, the ratio of NaOH solution/cassava, had impact on the S content. Increase in the level of factor F dramatically lead to increase of the S content. In contrast to E and F, the factors G and H had negative influence on the S content, i.e., the S content decreased with the increase of levels of factors G and H.

Adsorption of Pb^{2+} from Aqueous Solution

It was known that the adsorption capacity of the adsorbents varied according to the initial ions concentrations. Speaking in details, the amount of the absorbed ions increased while the removing percentages decreased with the increase of the initial metal concentrations. The adsorption capacity variation of the crosslinked cassava xanthate against initial metal concentration is presented in Figure 2(a). The adsorption amount of the ions increased with the increase of the initial concentration. The adsorption capacity was up to 950 mg/g (equaling to 4.59 mmol/g) as the initial concentration was 200 mg/L . In comparison with cellulose xanthate whose adsorption capacity of copper was less than 250 mg/g (equaling to 3.94 mmol/g),¹⁸ the crosslinked cassava xanthate exhibited unique large-amount adsorption, having the increment of up to 16% in the molar ratio. On the other hand, the removing percentages dropped as the concentration reached around 155 mg/L after a moderate decrease with the increase of the initial concentration. The observation was in agreement with findings of Bai et al. who studied the

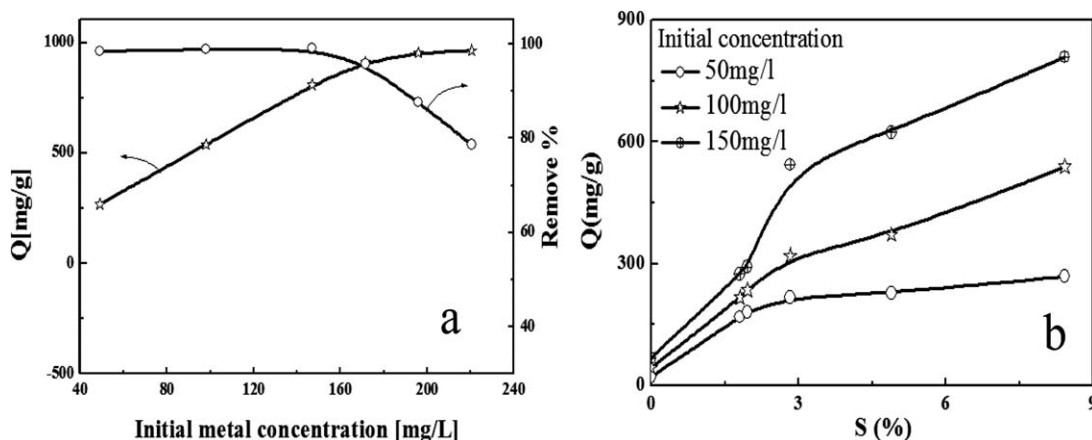


Figure 2. Plots of adsorption amount against initial metal concentrations (a), S content (b), and time at different temperatures (c).

adsorption of *Rhizopus nigricans* in 2001. They found that higher adsorption percentage was noted at lower initial concentrations of Cr ions, whereas the adsorption capacity of the biomass increased with the increase of ions concentration.⁷ The underlying mechanism was hypothesized as follows: the modified cassava had two types of binding sites toward the ions, i.e., highly active sites and lowly active sites. The former, such as hydroxyl, sulfur, cyano, and amino groups, participated in the adsorption as the concentration was low. Thus, the removing percentages were relatively high. When the concentration was increased, both the two types of sites worked together, leading to the total removing percentage decreased. The plots of

adsorption amount of the cassava xanthate against S content at different initial concentrations are shown in Figure 2(b). To be interesting, the cassava xanthate dramatically promoted its adsorption amount for those having relatively higher S content. There was obvious increase in the adsorption amount as the S content was in the range 2.5% and 3%. In particular, the increase magnified as the initial concentration increased from 50 mg/L to 150 mg/L. It may attribute to the chemical modification which was expected to increase the binding sites and enhanced the adsorption capacity of the cassava xanthate.

To further assess the adsorption efficiency of the cassava waste biomass, the adsorption dynamic process was monitored at

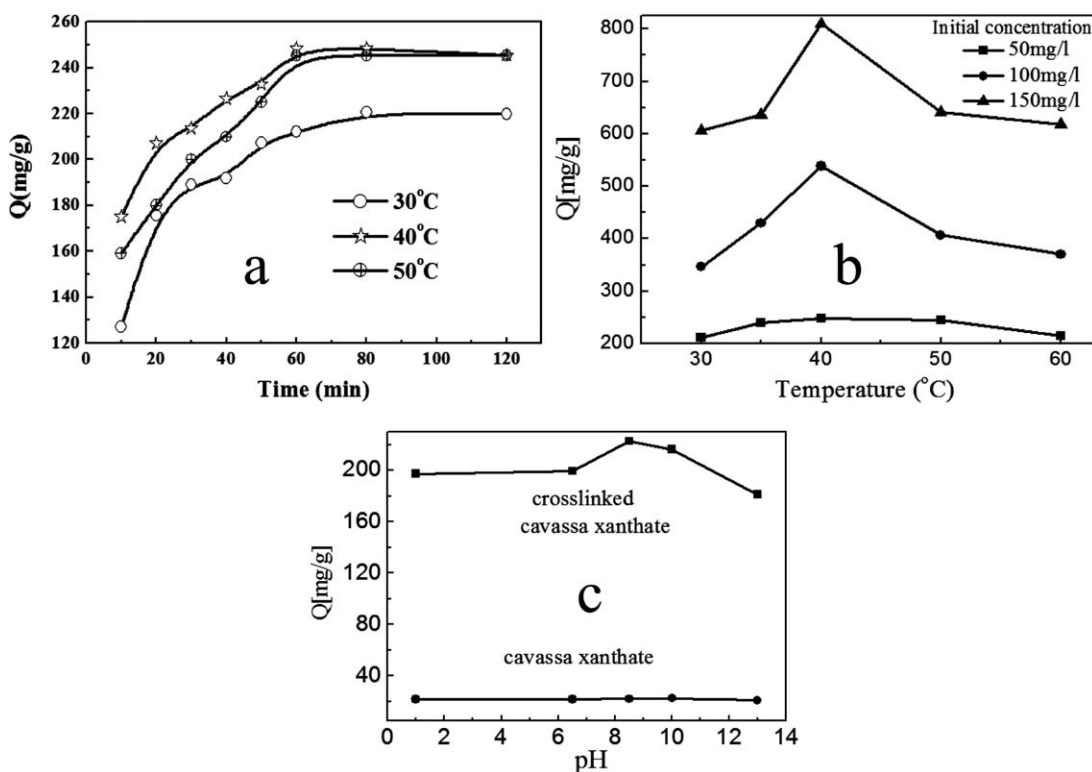


Figure 3. Absorption capacity against time (a), temperature (b), and pH (c).

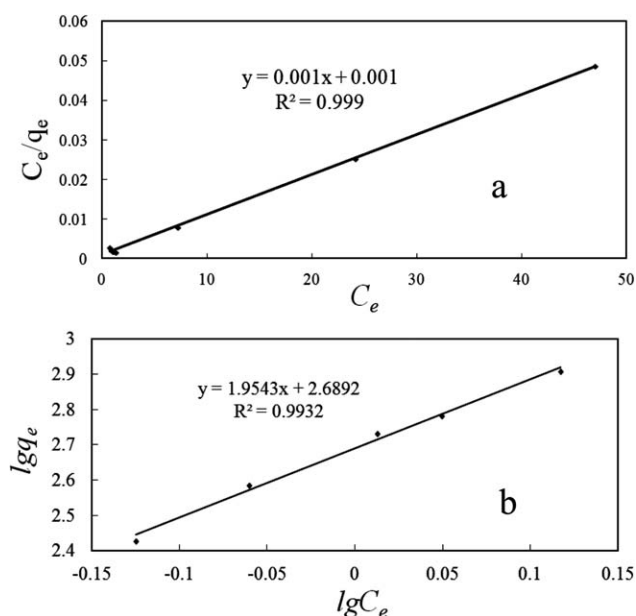


Figure 4. Langmuir ($C/Q = 1/Q_{\max}K_L + C$), (a) and Freundlich ($\ln Q = \ln k_F + (\ln C)/n$), (b) adsorption isotherms for Pb^{2+} removal by crosslinked cassava xanthate.

different temperatures with optimized pH value and initial metal concentration (pH = 8.5, $C_{Pb^{2+}} = 50$ mg/L), which is shown in Figure 3(a). It was found that the metal adsorption onto the biomass was pronouncedly rapid within the initial 1 h. Particularly, up to 70% of the ions were adsorbed within the initial 30 min. The adsorption reached the maximum amount within 60 min as the temperatures were 30°C, 40°C, and 50°C, showing greater efficiency than bio-sorbents reported in previous literature.⁷ It worth mentioning that neither high nor low temperature facilitated the adsorption. In comparison with 30°C and 50°C, 40°C was the most appropriate temperature for reaching the maximum adsorption. The phenomenon was in good agreement with the observation by plotting the adsorption against temperature at different initial metal concentrations which is shown in Figure 3(b).

There were two discrete stages for each of the three curves. In the first stage, the adsorption increased with the increase of the temperature in the range 30°C and 40°C. Maximum adsorptions were achieved as the temperature was 40°C. However, the adsorption decreased in the second stage, i.e., the temperature increased in the range 40°C and 60°C. When the temperatures were 30°C and 60°C, the adsorption achieved minimum values. Moreover, the contrast of adsorption between maximum and minimum values was greater as the aqueous solution had higher ions concentration. Increase of temperature may promote the movement of ions, facilitating binding among the metal ions and the cassava. However, the adsorption process of the cassava waste was determined to be exothermic,¹⁹ too high temperature made against the thermodynamic process of the physisorption, leading to the decrease of the adsorption. Thus, a middle level of 40°C was regarded as the optimum adsorption temperature in this study.

The plots of adsorption against pH values for cassava xanthate and crosslinked cassava xanthate are shown in Figure 3(c). The

pH variation had little influence on the adsorption of the cassava xanthate. By contrast, the adsorption capacity of the cross-linked cassava xanthate had a jump as the pH values were in the range 6.5 and 8.5. Subsequently, it decreased from the maximum to the minimum values as the pH values increased from 8.5 to 13. Given that the CS_2 applied for the crosslinking of the cassava xanthate was weakly acidic as dissolved in water, alkaline condition may favor the ionization of the resulting cassava xanthate. As a result, the crosslinked cassava xanthate obtained the maximum adsorption capacity at pH near to 8.

Adsorption Equilibrium and Kinetics

Langmuir and Freundlich models are commonly applied for numerical calculation of the adsorption.²⁰ The Langmuir sorption model, commonly used to estimate the maximum uptake of metal ions, is described by eq. (2),

$$C/Q = 1/Q_{\max}K_L + C \quad (2)$$

To obtain the Langmuir constant, a straight line of $1/Q$ versus $1/C$ was plotted which is shown in Figure 4(a). The isothermal constants and correlation coefficients are summarized in Table III. From the Langmuir isotherm, the adsorption affinity constant (K_L) and the maximum capacity (Q_{\max}) of Pb^{2+} forming a complete monolayer on the surface of the crosslinked cassava xanthates were estimated to be 861.50 L/g and 5000 mg/g, respectively. The maximum adsorption capacity provided evidence that chemical modification of cassava enhanced its potential adsorption ability. The value of K_L representing the affinity between sorbent and sorbate suggested that strong binding existed between ions and the cassava surface.

The linear Freundlich equation was used to evaluate the adsorption intensity n of Pb^{2+} toward crosslinked cassava xanthates.^{20,21}

$$Q = \ln k_F + (\ln C)/n \quad (3)$$

The constants $1/n$ and $\ln K_F$ were determined from a plot of $\ln Q$ versus $\ln C$ [shown in Figure 4(b)]. The isothermal Freundlich parameters are also summarized in Table III. The Freundlich adsorption coefficient K_F and the intensity n were determined to be 1.06 L/g and 6.91, respectively. The Langmuir equation was found to be more suitable, as indicated by the higher correlation coefficient ($r^2 = 0.998$) compared with that from Freundlich equation ($r^2 = 0.993$). The value of the Freundlich exponent, n , was greater than 1, which indicated that the Pb^{2+} adsorption increased for the crosslinked cassava xanthates as the ions concentration increased. Furthermore, the modeling fitness indicated that the adsorption of the crosslinked waste cassava

Table III. Linear Langmuir and Freundlich Isotherm Parameters for Pb^{2+} Sorption by Crosslinked Cassava Xanthate

Langmuir			Freundlich		
Q_{\max} (mg/g)	K_L	r^2	K_F	n	r^2
5000	861.50	0.998	6.91	1.06	0.993

Abbreviations: Q_{\max} , maximum adsorption capacity; K_L , Langmuir adsorption coefficient; K_F , Freundlich adsorption coefficient; n , adsorption intensity; r^2 , correlation coefficient.

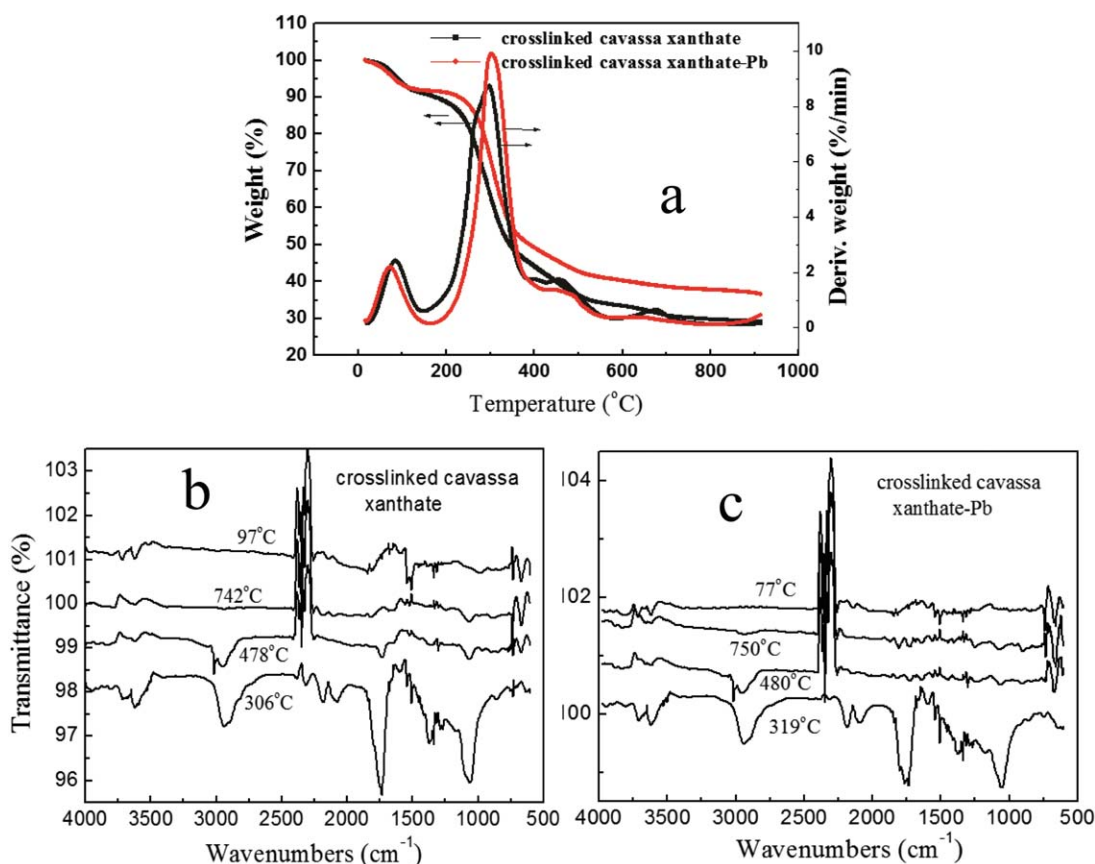


Figure 5. TGA-DTG measurements (a) and FTIR spectra of crosslinked cassava xanthate (b) and cassava xanthate-Pb (c) during pyrolysis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was mainly under single physical-chemical mechanism, rather than multimechanisms, for instance, deposition of the Pb in the form of $\text{Pb}(\text{OH})_2$.

Thermal Properties of Crosslinked Cassava Xanthate

Thermal gravimetric analysis (TGA)-FTIR analysis is a useful tool to measure the pyrolysis of biomass.²² The TGA-DTG curves of the crosslinked cassava xanthate and crosslinked cassava xanthate-Pb are shown in Figure 5(a).

There were four obvious peaks locating at around 90°C, 300°C, 480°C, and 740°C in the DTG curves, respectively, indicative of multistep weight loss of the samples during pyrolysis.^{23–25} The first weight loss peak could be assigned as evaporation of water content in the samples, which followed by a prominent peak locating at round 300°C attributing to the cassava decomposition. It was reported that hemicellulose was decomposed mainly between 150°C and 350°C, cellulose was decomposed between 275°C and 350°C and lignin undergone gradual decomposition between 250°C and 500°C.²⁶ Therefore, the prominent peak was probably due to the decomposition of cellulose and the peak locating at 480°C was due to the decomposition of lignin.²⁷ The residual weights of the crosslinked cassava xanthate and cassava xanthate-Pb at high temperature up to 800°C were 30% and 37%, respectively. The variation on the residual weight resulted from the heavy metal adsorption. FTIR provided further evidence that the weight loss of the samples in high temperature

range derived from degradation of cellulose, starch, hemicellulose, and lignin, which are shown in Figure 5(b,c). When the temperature was above 450°C, the crosslinked cassava xanthate and cassava xanthate-Pb lost another 5.8% and 4.6% of weights, due to carbonization process of samples. The adsorption peaks could be assigned as follows²⁸: CO_2 at 2359 cm^{-1} ; CO at 2180 cm^{-1} and 2118 cm^{-1} ; H_2O at 3964–3500 cm^{-1} ; and 1500–1300 cm^{-1} ; a variety of saturated hydrocarbons and unsaturated hydrocarbons at 3000–2800 cm^{-1} ($-\text{CH}_3$ and $-\text{CH}_2$) and 3016 cm^{-1} ($\text{CH}=\text{CH}$ of dutrex); hydrocarbons, carboxylic acids, alcohols, ketones, aldehydes, and other macromolecules at 1900–1650 cm^{-1} ($\text{C}=\text{O}$) and 1300–900 cm^{-1} ($\text{C}-\text{O}$ and $\text{C}-\text{C}$). Because the adsorbed Pb ions were free for characteristic signals in the FTIR measurement, both of the two spectra were similar to each other at certain extent.

Regeneration of Crosslinked Cassava Xanthate as Pb^{2+} Adsorbent

The crosslinked cassava xanthate could be regenerated by immersion into aqueous solution with certain pH values. It was known that dilute acid solution was helpful for desorption of metal ions from the cassava waste biomass and recycling the metals.⁹ In this study, the plot of desorption percentages against acidity of the solution is presented in Figure 6.

The desorption significantly increased from 2.1% to 30.9% as the pH values of the solution decreased from 13 to 2.

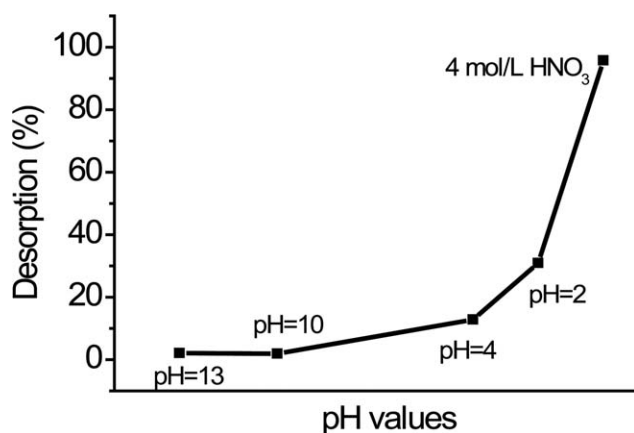


Figure 6. Plot of desorption against acidity of the solution.

Furthermore, the desorption was up to 95.7% when the sample was immersed into 4 mol/L HNO₃ solution. Hence, 4 mol/L HNO₃ solution was used for cyclic regeneration of the CCX-Pb. It was found that the adsorption in the first, second, and third cycles were 97.3%, 60.0%, and 52.1%, respectively.

CONCLUSIONS

The cassava xanthate with optimized crosslinking efficiency and S content could be obtained by tailoring the components ratio in the synthesis process. The adsorption capacity of the cross-linked cassava xanthate for Pb²⁺ ions removal was affected by multiple parameters. High initial ions concentration and S content, weak alkali condition, and moderate temperature resulted into optimized adsorption. The adsorption equilibrium and kinetics could be fitted by Langmuir and Freundlich models. Crosslinking promoted the adsorption amount and efficiency. Multistage weight loss with decomposition occurred during pyrolysis. The cassava biomass adsorbing Pb²⁺ ions could be regenerated by immersion into dilute HNO₃ solution.

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