

암모늄티오우레아로 변형된 Walnut 껍질의 합성 및 분석과 수용액에서 납(II) 흡착 특성

Guangtian Liu[†] and Yundong Gao

Hebei Key Laboratory of Applied Chemistry, School of Environmental and Chemistry Engineering, Yanshan University
(2015년 9월 1일 접수, 2015년 11월 17일 수정, 2015년 11월 28일 채택)

Synthesis and Characterization of Aminothiourea Modified Walnut Shell and Its Adsorption for Pb(II) Ions from Aqueous Solution

Guangtian Liu[†] and Yundong Gao

Hebei Key Laboratory of Applied Chemistry, School of Environmental and Chemistry Engineering,
Yanshan University, Qinhuangdao, 066004, China

(Received September 1, 2015; Revised November 17, 2015; Accepted November 28, 2015)

Abstract: A novel, green and easy regeneration biosorbent, aminothiourea modified walnut shell (AMWNS), was synthesized, and its potential for removal of Pb(II) ions was also investigated. The AMWNS was synthesized with epichlorohydrin and aminothiourea as an etherifying agent and a modified monomer, respectively, and was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and X-ray diffraction (XRD). The influences of pH (3-11) and adsorbent dosage (0.5-2.5 g/L) on adsorption capacity of AMWNS were investigated. The maximum Pb(II) ions adsorption capacities (Q_m) calculated by best fitting model (Langmuir) were 46.25 mg/g at 298 K. Thermodynamic studies demonstrated adsorption process by AMWNS was spontaneous and endothermic. Furthermore, the regeneration capability of AMWNS implied AMWNS was a cheap, excellent biosorbent for Pb(II) ions removal in wastewater treatment.

Keywords: adsorption, aminothiourea modified walnut shell (AMWNS), Pb(II) ions, thermodynamics.

Introduction

With the development of the industry, heavy metals released into the environment, which pose a significant threat to the ecosystem and, consequently, human health because of their toxicity and persistence.¹ Thus, it is crucial that heavy metals should be removed from wastewater effectively before being discharged into the environment. Conventional treatment technologies used for heavy metal removal mainly include ion exchange, filtration, membrane separation, chemical precipitation, solvent extraction, and reverse osmosis, etc..²⁻⁴ However, these technologies generally cannot perfectly follow the increasingly stringent regulations on the heavy metal discharge in a cost effective manner.⁵ An important drawback of precipitation techniques is significant sludge production. Although

ion exchange is considered to be an alternative method for removal of Pb(II) ions, it is expensive and the majority of ion exchangers have poor selectivity for them. Therefore the identification of feasible technologies for heavy metal separation and removal from aqueous solutions have become an urgent problem.

Compared to other techniques, adsorption is considered to be among the most favorable processes because of its simplicity, ease of operation, regeneration capacity sludge-free operation, and low cost for industrial application.⁶⁻⁸ Consequently, the development of new and more effective adsorbents has become essential.

Various materials have been studied to determine their efficiency in heavy metal adsorption, including activated carbon, agricultural by-products, nutshells, biomaterials.⁹⁻¹² However, the adsorption performance of most of these materials has been, for the most part, unsatisfactory. To further improve adsorption efficiency, the discovery of application of more efficient adsorbents seems necessary. In recent years, modified

[†]To whom correspondence should be addressed.

E-mail: gtl@desire@163.com

©2016 The Polymer Society of Korea. All rights reserved.

biomass materials including agricultural residue have been extensively applied for heavy metal ions removal due to low cost, renewable and easy disposal.¹³⁻¹⁵

Walnut shell is a forestry residue, obtained easily, cheap, nontoxic, and biodegradable. Thiosemicarbazide contained multiple adsorption groups, and it was a cheap and water soluble monomer, the grafting reaction occurred in aqueous solution, which didn't lead to pollution of the environment. So, in this study, a green, non-toxic, biodegradable adsorbent-chemically modified walnut shell with aminothiourea (AMWNS) was synthesized, characterized and used for the Pb(II) ions removal. The influences of pH and adsorbent dose on Pb(II) ions absorption were investigated. The mechanism of Pb(II) ions absorption by AMWNS was deduced with isotherms and thermodynamics results. Furthermore, desorption and reusability of the modified adsorbents were evaluated after adsorption of Pb(II) ions. The aim of this study is to provide a cheap, excellent biosorbent of AMWNS for Pb(II) ions removal in wastewater treatment.

Experimental

Materials. Walnut shell (WNS) species which were collected from Shijiazhuang, China. Epichlorohydrin, HCl, Pb(NO₃)₂ and NaOH were obtained from Tianjin Guangfu technology development co., LTD (Tianjin, P. R. China). Aminothiourea was purchased from Beijing chemistry factory (Beijing, P. R. China). All other commercial chemicals were of analytic reagent grade and used without further purification and all solutions used in the experiments were prepared with deionized water.

Synthesis of Modified WNS. Prior to modification, the walnut shell (WNS) was boiled for 60 min to get rid of the pulp and residual seed capsule. Then, it was rinsed thoroughly with deionized water to wipe off fly ash, residual adhesive flesh and other inorganic impurities. The clean WNS was dried for over 24 h at 105 °C until constant weight, then the WNS were ground in a high speed grinder and the resulting crumbs were sieved to obtain size of smaller than 100 m. The sieved WNS was stored in a desiccator for further use or modification. The modification process of WNS was performed as follows: firstly, 15 mL of NaOH (1.25 M) was blended with 10 mL epichlorohydrin on a shaker at room temperature. Then, WNS (1.0 g) was immersed into the solution at 40 °C for 30 min equipped with thermostat. After the mixtures washed several times to the eluent pH neutral, the obtained materials

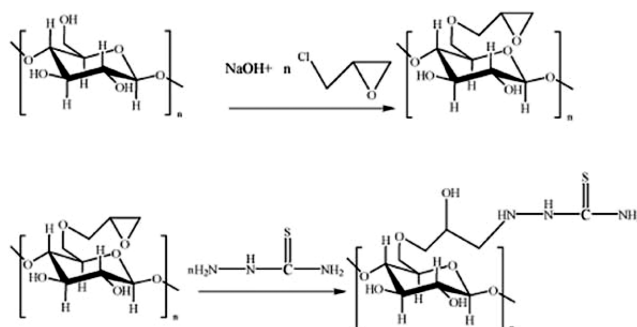


Figure 1. Associated reactions of the modification process.

(called M₁-WNS) was dried at 65 °C until constant weight. Afterwards, the solution with 15 mL of NaOH (0.125 M) and aminothiourea (1.0 g) was added into M₁-WNS powder captured previously. The mixtures were stirred with constant temperature magnetic heating stirrer at 65 °C for 60 min, and subsequently were washed with deionized water to the eluent pH neutral. Finally, the washed powder was dried in vacuum at 65 °C for 3 h, grinding sieved to get amino-modified walnut shell (AMWNS). The modification process involved a series of associated reactions is illustrated in Figure 1.

Characterization Methods. Fourier transform infrared spectroscopy (FTIR) of type Nicolet380 spectrometer system (Nicolet Company, U.S.A.) was used to study whether or not aminothiourea was grafted onto WNS. Infrared spectra were obtained by the KBr disc technique.

Scanning electron microscopy (SEM) images were observed on a Hitachi S-3400N scanning microscope (Hitachi, Japan). Each WNS sample was suspended in a bottle in which there was a small amount of ethanol under ultrasound. The sample was mounted on glass plates and dried for removal of the ethanol, followed by coating with a thin layer of gold in a vacuum before examination.

The XRD measurement was conducted using a RigakuD-max-2550/PC diffractometer (Rigaku Inc., Tokyo, Japan). The XRD pattern was obtained using CuK α radiation with an incident wavelength of 0.1542 nm under a voltage of 40 kV and a current of 200 mA. The scan rate was 4 °/min.

Absorption Experiment. The adsorption experiments were carried out in a series of 100 mL Erlenmeyer flasks containing the desired dose of AMWNS and 50 mL of Pb(NO₃)₂ solution at the desired concentration in a shaking bath. The effect of initial solution pH on the removal of Pb(II) ions was performed in the range of 3-11. The pH was adjusted with 0.1 M HCl or 0.1 M NaOH before adding the adsorbent. Adsorbent doses varied from 0.5 to 2.5 g/L were conducted to investigate the

influences of adsorbent content on Pb(II) ions removal. Besides, the adsorption equilibrium studies were analyzed at initial Pb(II) ions concentration ranged from 20 to 160 mg/L (pH=7), and different temperatures of 293, 298, 303, 308 and 313 K were considered for thermodynamic studies. During the batch adsorption studies, the flasks containing adsorbent and adsorbate were agitated with 180 rpm for 2.0 h in a water bath constant temperature oscillator (SHZ-82, Jintan jingbo experimental instrument company, China). Afterwards, the flasks were withdrawn and the residual adsorbate concentrations were measured by atomic absorption spectrometer (Z-2000, Hitachi Limited Company, Japan). All tests were performed with three replicates and the mean values were used for subsequent analysis.

Desorption and Regeneration Studies. To regenerate the used AMWNS for further Pb(II) ions removal, desorption and regeneration experiments were conducted in batch mode. Firstly, the 40.02 mg/g Pb(II) ions loaded AMWNS (Pb²⁺-AMWNS) was obtained by immersing 0.02 g adsorbent into 20mL Pb(II) ions solution. Subsequently, the Pb(II)-AMWNS was placed into 0.1M HCl solution, and then was shaken on water bath constant temperature oscillator at room temperature for 2 h, and the sorbent was removed from the solution and washed with deionized water. Furthermore, the reusability of the regenerated AMWNS was tested by executing further 3 consecutive adsorption-desorption experiments at the same adsorption conditions.

Calculations. The lead removal efficiency and adsorption capacity of WNS and AMWNS were calculated from the following expressions:

$$Q_e = (C_0 - C_e) \times V/M$$

$$\text{Efficiency (\%)} = (C_0 - C_e)/C_0 \times 100\%$$

Where C_0 is the initial metal ions concentration (mg/L), C_e is the balance metal ion concentration (mg/L). V (L) is the volume of solution; M (g) is the mass of adsorbent; and Q_e (mg/g) is the equilibrium adsorption capacity.

Results and Discussion

FTIR and XRD Analysis of Modified WNS. The FTIR spectrum of original WNS and the modified WNS are illustrated in Figure 2. The pronounced peak located at 3430 cm⁻¹ is assigned to the O-H stretching vibration of hydroxyl groups and N-H stretching vibrations. The bands at around 2935 cm⁻¹

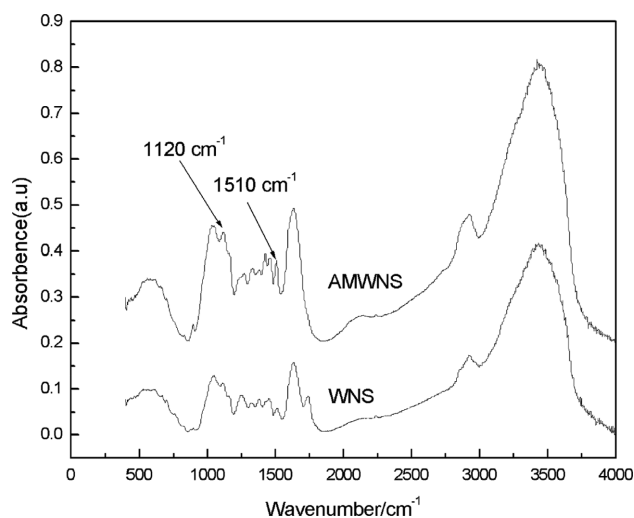


Figure 2. FTIR of walnut shell (WNS) and amino modified walnut shell (AMWNS).

are attributed to C-H stretching vibrations in methyl and methylene groups. The peak at 1247 cm⁻¹ and an intense band at around 1038 cm⁻¹ can be attributed to C-O stretching vibrations in alcohols, phenols, or ether or ether groups. Compared to the original WNS, in the FTIR spectrum of the modified WNS, the typical absorption peak at 1510 cm⁻¹ represents C=S which originates from thiosemicarbazide. The new band generated at 1120 cm⁻¹ can be ascribed to C-N bend vibrations. The results provide the evidence of the WNS being grafted with aminothiourea.

The effect of graft copolymerization on the crystallinity of

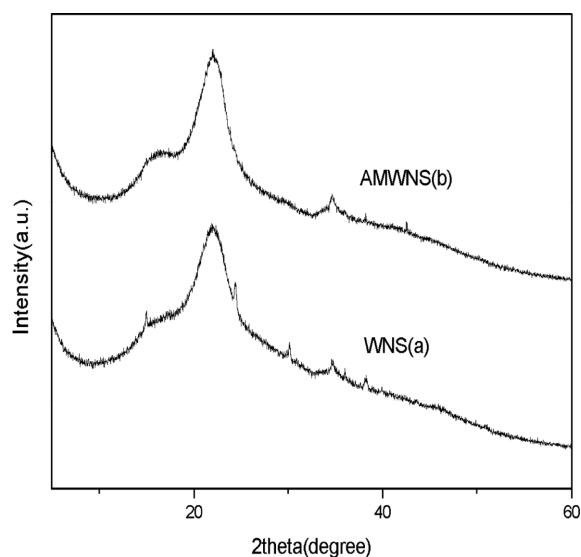


Figure 3. XRD spectras of walnut shell (WNS) and amino modified walnut shell (AMWNS).

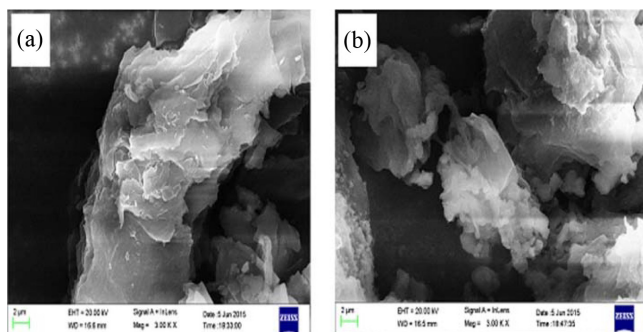


Figure 4. SEM pictures of (a) original walnut shell (WNS); (b) amino modified walnut shell (AMWNS).

WNS (a) and AMWNS (b) was studied by XRD pattern (Figure 3). The original WNS shows scattering at $2\theta=15.0^\circ$, 22.1° , 24.5° , 30.2° , 34.9° , 38.3° , which are characteristic peaks of WNS. The absence of the peak at $2\theta=15.0^\circ$, 22.1° , 30.2° , 38.3° in AMWNS indicates that the intensity and sharpness of the diffraction decrease, confirming the decrease in crystallinity. The possible explanation was that aminothiourea grafted on WNS destroyed original ordered structure of WNS.

The results above provide the evidence of the WNS being grafted with thiosemicarbazide.

SEM Image Analysis. The morphological microstructures and surface characteristics of WNS and AMWNS were observed with SEM (Figure 4). The original WNS particles (Figure 4(a)) show smooth on the surface, while the surfaces of AMWNS (Figure 4(b)) leads to an altered uneven surface on the particles, which increased the surface area and well facilitated the adsorption of lead ions.

Influence of pH on Pb(II) Ions Removal. The solution pH has been consistently considered the most important variable in sorption investigations as it controls the surface charge of adsorbents, the degree of ionization, and the speciation of adsorbate species.^{16,17} The influence of pH (3-11) on Pb(II) ions adsorption is illustrated in Figure 5. Significant rises in removal of lead ions occurred with increases in solution pH up to 7. The reduced metal uptake witnessed at low pH values may have been due to the higher concentration and mobility of H^+ ions, which result in becoming more $-NH_3^+$, $-OH_2^+$ or $C=SH^+$ in the surface of AMWNS, electrostatic repulsion between $-NH_3^+$, $-OH_2^+$ or $C=SH^+$ with Pb^{2+} enhanced, so chelation of $-NH_2$, $-OH$ or $C=S$ with Pb^{2+} was suppressed.¹⁸ When solution pH was 7, the adsorption capacity of AMWNS on Pb(II) ions reached about 40.02 mg/g. This could be attributed to zeta potential changes in surface electric charge of the

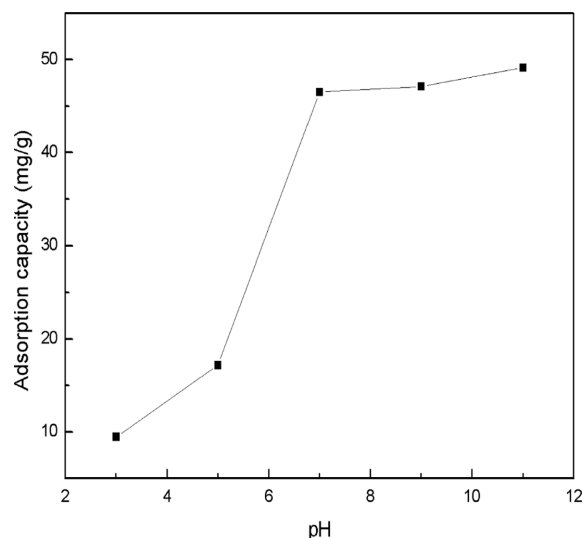


Figure 5. Effects of pH on adsorption capacity of Pb(II) ions by WNS and MWNS (conditions: temperature, $25\pm 1^\circ C$; adsorbent dosage, 0.5 g/L; react time, 120 min; initial Pb^{2+} concentration, 50 mg/L).

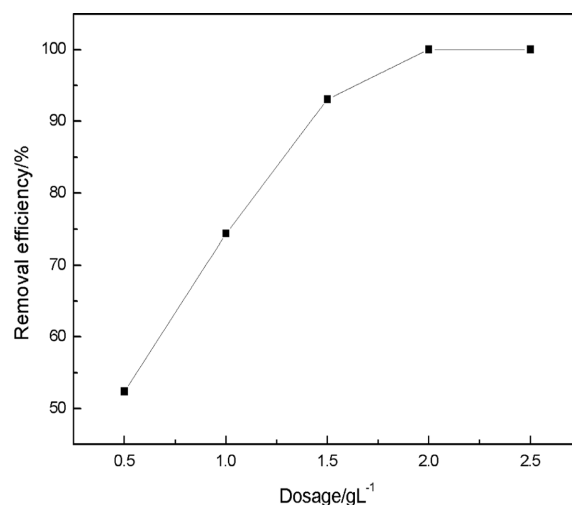


Figure 6. Effects of removal efficiency of Pb(II) ions by WNS and MWNS (conditions: temperature, $25\pm 1^\circ C$; pH=7; react time, 120 min; initial Pb^{2+} concentration, 50 mg/L).

AMWNS.¹⁹

At higher pH values, lower H^+ concentration along with a greater negatively-charged adsorbent surface result in greater attraction of metal cations. In addition, the active site of AMWNS becomes free $-NH_2$, $-OH$ or $-C=S$, which can chelate on Pb^{2+} easily. However, an increase in lead removal was observed at high pH, which could be due to the formation of several hydroxide species of Pb(II) ions which was precipitated.^{20,21}

Influence of Adsorbent Dosage on Pb(II) Ions Removal.

The influence of dosage of original WNS and AMWNS on Pb(II) ions removal efficiency is showed in Figure 6. For the AMWNS, the adsorption removal efficiency of Pb(II) ions increased significantly (from 52.38 to 99.9%) when the adsorbent dosage was gradually raised from 0.5 to 2.5 g/L. As the adsorbent dosage increased, a substantial increase in available adsorption sites resulted in a high percentage of adsorption.

Adsorption Isotherms. Adsorption isotherms are significant prerequisites to establish the most appropriate relationship between adsorbate and adsorbent, and are critical in optimizing the design of an adsorption system for Pb(II) ions removal. Lots of isotherm equations can be utilized to establish the correlation, such as Langmuir, and Freundlich models.^{22,23} The corresponding isotherm equations are represented as:

$$\text{Langmuir isotherm: } \frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad (1)$$

Where C_e (mg/L) is the ultimate concentration of Pb(II) ions at equilibrium and Q_e (mg/g) is the corresponding adsorption capacity. Q_m (mg/g) is the theoretical maximum monolayer Pb(II) ions adsorption capacity of adsorbent, and K_L (L/mg) is the Langmuir isotherm coefficients related to the free energy of adsorption. The straight lines were given by plotting C_e/Q_e versus C_e , as shown in Figure 7(A), which gave the values of K_L and Q_m in Table 1 according to the intercept and slope of these lines, respectively.

$$\text{Freundlich isotherm: } \ln Q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (2)$$

Where K_F ((mg/g)(L/mg)^{1/n}) and $1/n$ are the adsorption constants of Freundlich model generally related to the strength of interaction between adsorbate and sorbent. The linearized Freundlich isotherms was shown in Figure 7(B) and the parameters were also shown in Table 1. The low value of the linear correlation coefficient R^2 (0.655) indicated the unsuitability of Freundlich isotherm model. The values of R^2 for Langmuir model (0.998) were high, indicating that this model could be used to characterize the equilibrium adsorption. The results of

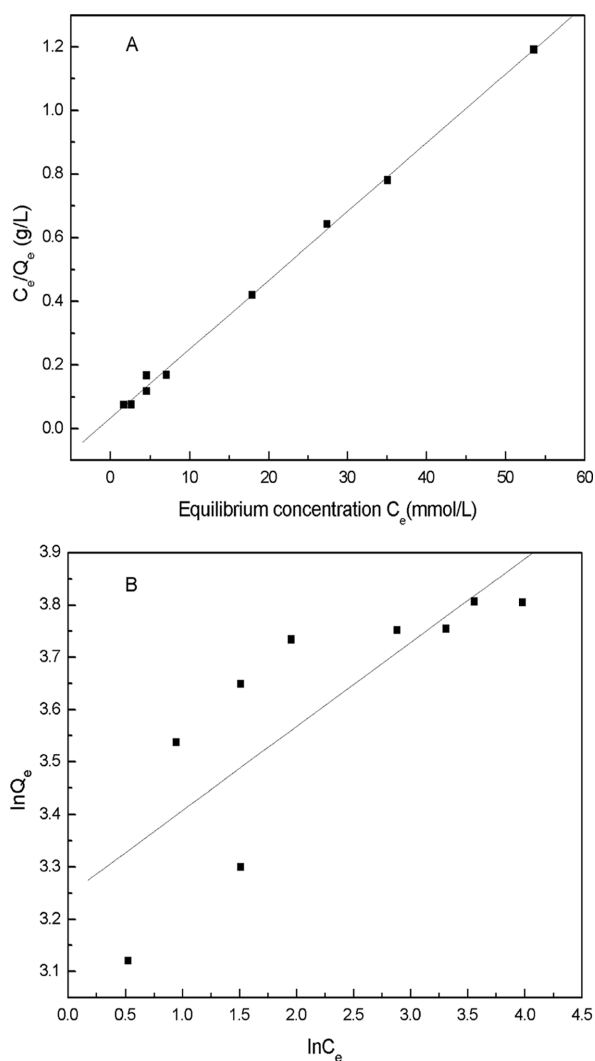


Figure 7. Isotherm models for Pb(II) ions adsorption onto AMWNS (A) Langmuir model; (B) Freundlich model.

Langmuir model demonstrated that homogeneous monolayer Pb(II) ions was covered onto AMWNS particles.²⁴ Furthermore, the results indicated that the adsorption of Pb(II) ions was a dynamic chemisorption process by the adsorption affinity in terms of surface functional groups and bonding energy.²⁵ The maximum adsorption capacities (Q_m) of AMWNS for Pb(II) ions were 46.25 mg/g and were almost the same as

Table 1. Adsorption Isotherm Constants for Pb²⁺ Adsorption onto the AMWNS

$Q_e^*/\text{mg}\cdot\text{g}^{-1}$	Langmuir			Freundlich		
	Q_m^{**} (mg·g ⁻¹)	K_L (L·mg ⁻¹)	R^2	K_F	n	R^2
44.99	46.25	0.648	0.998	1.174	6.234	0.655

*Experimental data. **Calculated data.

those of experiment dates (44.99 mg/g).

A dimensionless constant called separation factor (R_L) was applied to evaluate the suitability of an adsorption process, and it was defined as the following eq. (3):²⁶

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

where C_0 (mg/L) is the initial Pb(II) ions concentration in solution and K_L (L/mg) is the Langmuir isotherm coefficients related to the free energy of adsorption. The values of R_L (0.0019–0.0096) at 298 K was in the range of 0–1, implying the sorption process belonging to a favorable uptake of Pb(II) ions by AMWNS.²⁷

Thermodynamics Studies. To better understand the influences of temperature on the adsorption of Pb(II) ions on MWNS, three thermodynamic parameters of the adsorption process, including the changes in enthalpy (ΔH), entropy (ΔS) and free energy (ΔG), were investigated. The changes in enthalpy and entropy were determined with the equations below:²⁸

$$\ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4)$$

Where K_D (L/mol) is thermodynamic adsorption equilibrium constant and calculated by eq. (5) below. Here, T is the absolute temperature and R is the gas constant valued 8.314 J/(mol K). The values of ΔH and ΔS were determined from the slope and intercept of the fitted curve (Figure 8), respectively.

$$K_D = \frac{Q_e}{C_e} \quad (5)$$

Where Q_e is the equilibrium Pb²⁺ concentration on the adsorbent (mg/L) and C_e is the equilibrium Pb²⁺ concentration in solution (mg/L).

The Gibbs free energy of adsorption (ΔG) subsequently determined from the identified parameters ΔH and ΔS by eq. (6).²⁹

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

The obtained values of thermodynamic parameters for Pb(II) ions adsorption onto AMWNS are listed in Table 2. As it can be seen from Table 2, ΔH values are found to be positive for all cases due to adsorption is endothermic. Although there are no certain criteria related to the ΔH values that define the adsorption type, it is obvious from the ΔH value obtained for

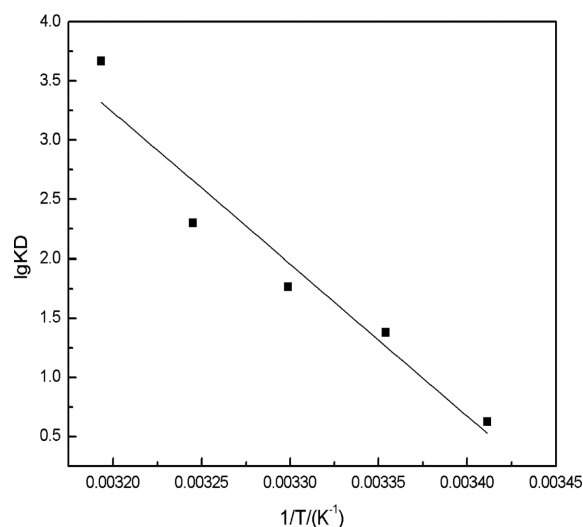


Figure 8. $\log K_D \sim 1/T$ for AMWNS (Pb²⁺=44.68 mg/L; pH=7; t=2 h; the dose of AMWNS is 1.0 g/L).

Table 2. Thermodynamic Parameters of Adsorption of Pb²⁺ on AMWNS

T (K)	K_D (L/g)	ΔG (KJ·mol ⁻¹)	ΔH (KJ·mol ⁻¹)	ΔS (J·mol ⁻¹ ·K ⁻¹)
293.15	1.87	-95.05		
298.15	3.98	-96.89		
303.15	5.83	-98.73	12.82	367.98
308.15	9.99	-100.57		
313.15	39.15	-102.41		

Pb(II) that chemisorption also takes part in the adsorption process with chelating effects of the functional groups available on the surface of AMWNS. An increase in temperature would lead to an increase in adsorbate on AMWNS.¹⁹ The positive ΔS corresponded to an increase in the degrees of freedom of the solid–liquid interface during adsorption process of Pb(II) ions onto AMWNS. On the other hand, Negative values of ΔG indicate the spontaneous nature of the reaction. The values of ΔG become more negative with increase temperature, which means that the adsorption process is more favorable at high temperature.

Desorption and Regeneration Studies. The reversibility of the adsorption process was also investigated. Desorption studies are helpful to explore the possibility of recycling the sorbents and recovery of Pb(II) ions. The results demonstrated that the Pb(II) ions adsorption capacity of the modified adsorbent decreased slightly after 3 consecutive adsorption/desorption (the removal efficiency maintained above 90%).

Conclusions

In this study, a novel amino walnut shell (AMWNS) was prepared by grafting aminothiourea onto walnut shell backbone. The characterization using various instruments demonstrated that aminothiourea was successfully grafted onto walnut shell backbone. Further, adsorption properties of AMWNS for Pb(II) ions from aqueous solution were investigated. The pH experiments showed that maximum adsorption occurred at pH 7-8. When the adsorbent dosage was 2 g/L, removal efficiency was the highest. The adsorption process can be well described by Langmuir isotherm with a maximum adsorption capacity 46.25 mg/g at 298 K. The adsorption isotherms indicated that the surfaces of AMWNS were distributed by a homogeneous monolayer of Pb(II) ions with a dynamic chemisorption process. Furthermore, the values of ΔG become more negative with increase temperature, which indicates that the adsorption process is more favorable at high temperature. The results demonstrated that AMWNS had a good regeneration ability. This research is worthwhile and it can be foreseen with a great prospect in Pb(II) ions removal in wastewater treatment.

References

1. Y. Liu, M. Chen, and Y. Hao, *Chem. Eng. J.*, **218**, 46 (2013).
2. S. A. Kim, S. K. Kamala, K. Lee, Y. Park, P. J. Shea, W. Lee, H. Kim, and B. Oh, *Chem. Eng. J.*, **217**, 54 (2013).
3. F. Googerdchian, A. Moheb, and R. Emadi, *Chem. Eng. J.*, **200**, 471 (2012).
4. S. Lee, C. Laldawngliana, and D. Tiwari, *Chem. Eng. J.*, **195**, 103 (2012).
5. V. K. Gupta, S. Agarwal, and T. A. Saleh, *Water Res.*, **45**, 2207 (2011).
6. G. P. Rao, C. Lu, and F. Su, *Sep. Purif. Technol.*, **58**, 224 (2007).
7. A. Z. M. Badruddoza, A. S. H. Tay, P. Y. Tan, K. Hidajat, and M. S. Uddin, *J. Hazard. Mater.*, **185**, 1177 (2011).
8. S. Saha and P. Sarkar, *J. Hazard. Mater.*, **227**, 68 (2012).
9. D. Lan, D. Bing, D. Lanlan, C. Qiong, Y. Yong, and D. Yang, *Polym. Korea.*, **38**, 557 (2014).
10. S. Chen, Q. Yue, B. Gao, Q. Li, X. Xu, and K. Fu, *Bioresour. Technol.*, **113**, 114 (2012).
11. J. S. Cao, J. X. Lin, F. Fang, M. T. Zhang, and Z. R. Hu, *Bioresour. Technol.*, **163**, 199 (2014).
12. E. M. Choi, B. G. Son, C. S. Lee, and T. S. Hwang, *Polym. Korea.*, **33**, 52 (2009).
13. L. C. Hsu, S. L. Wang, Y. C. Lin, M. K. Wang, P. N. Chiang, J. C. Liu, W. H. Kuan, C. C. Chen, and Y. M. Tzou, *Environ. Sci. Technol.*, **44**, 6202 (2010).
14. D. Bulgariu and L. Bulgariu, *Bioresour. Technol.*, **103**, 489 (2012).
15. M. Inyang, B. Gao, Y. Yao, Y. Xue, A. R. Zimmerman, P. Pullammanappallil, and X. Cao, *Bioresour. Technol.*, **110**, 50 (2012).
16. A. S. E. Abdel, Y. H. Gad, and A. M. Dessouki, *J. Hazard. Mater.*, **129**, 204 (2006).
17. A. Naghizadeh, S. Nasser, and S. J. Nazmara, *Environ. Health Sci. Eng.*, **8**, 317 (2011).
18. M. Mohammad, T. K. Sen, S. Maitra, and B. K. Dutta, *Water Air Soil Pollut.*, **215**, 609 (2011).
19. S. H. Chen, Q. Y. Yue, B. Y. Gao, and X. Xu, *J. Colloid Interface Sci.*, **349**, 256 (2010).
20. A. K. Meena, K. Kadirvelu, G. K. Mishra, C. Rajagopal, and P. N. Nagar, *J. Hazard. Mater.*, **150**, 604 (2008).
21. A. Ahmad, M. Rafatullah, O. Sulaiman, M. H. Ibrahim, Y. Y. Chii, and B. M. Siddique, *Desalination*, **247**, 636 (2009).
22. D. H. Ding, Y. X. Zhao, S. J. Yang, W. S. Shi, Z. Y. Zhang, Z. F. Lei, and Y. N. Yang, *Water Res.*, **47**, 2563 (2013).
23. H. Parab and M. Sudersanan, *Water. Res.*, **44**, 854 (2010).
24. G. Yuvaraja, N. Krishnaiah, M. V. Subbaiah, and A. Krishnaiah, *Colloids Surf. B: Biointerfaces*, **114**, 75 (2014).
25. Y. F. Feng, D. D. Dionysiou, Y. H. Wu, H. Zhou, L. Z. Yang, L. H. Xue, and S. Y. He, *Bioresour. Technol.*, **138**, 191 (2013).
26. C. L. Xia, Y. Jing, Y. Z. Jia, D. Y. Yue, J. Ma, and X. J. Yin, *Desalination*, **265**, 81 (2011).
27. M. Bhaumik, R. McCrindle, and A. Maity, *Chem. Eng. J.*, **228**, 506 (2013).
28. J. W. Lin, Y. H. Zhan, Z. L. Zhu, and Y. Q. Xing, *J. Hazard. Mater.*, **193**, 102 (2011).
29. R. Gong, S. X. Zhu, D. Zhang, J. Chen, S. J. Ni, and R. Guan, *Desalination*, **230**, 220 (2008).