Cellulose (2022) 29:9819–9830
https://doi.org/10.1007/s10570-022-04869-z

ORIGINAL RESEARCH

Preparation of efficient heavy metal adsorbent based on walnut shell and adsorption for Pb(II) ions from aqueous solution

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Received: 24 May 2022 / Accepted: 26 September 2022 / Published online: 1 October 2022

Abstract An efficient heavy metal absorbent, amino-terminated hyperbranched polymer modified walnut shell (FWNS) was prepared. The adsorption behavior for Pb(II) ions from aqueous solution was also discussed. The FWNS was prepared using an amino-terminated hyperbranched polymer (ATHBP) as modifying agent and glycidyl methacrylate(GMA) as the grafting bridge. The FWNS was characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Scanning electron microscope (SEM). The adsorption capacity of FWNS for Pb(II) was investigated at different adsorbent dosages (0.25–2.5gL^{-1}) and pH (from 2.0 to 6.0). The result indicated that the absorbent had good adsorption capacity over a wide pH range (2.0–6.0). The maximum Pb(II) ions adsorption capacity (Q_m) obtained by a Langmuir fitting model was 1250.00 mg/g at 293 K. The adsorption kinetics fitted the pseudo-second-order equation. The adsorption of FWNS for Pb(II) ions was an endothermic reaction and spontaneous process. Furthermore, the result shows FWNS has excellent regeneration.

Keywords Amino-terminated hyperbranched polymer(ATHBP) · Walnut shell · Pb(II) ions · Adsorption isotherms · Kinetics · Regeneration

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Introduction

In recent years, with the development of modern industry, groundwater resources have been polluted by heavy metal wastewater emissions, posing a serious threat to people's daily life and health (Liu et al. 2013a, b). Therefore, it is crucial to seek effective treatment methods to reduce heavy metal concentration in wastewater. The conventional heavy metal wastewater treatment method (Kim et al. 2013; Googerdchian et al. 2012; Lee et al. 2012; Li et al. 2011; Jin et al. 2011) is a chemical method. It is a simple process with low cost but it is easily to produce large amounts of sediment and secondary pollution. Membrane filtration, which has often been used in recent years, has a good effect on removal of heavy metal ions, but the processing efficiency of membranes greatly decrease with use, and need to be replaced regularly. Polymeric adsorbent have a stronger ability to adsorb heavy metals, but the monomers are toxic, refractory and expensive.

A number of studies have described modified natural polymers as heavy metal adsorbent (Lo et al.

2012, Vaghetti et al. 2009, Xie et al. 2011, Chen et al. 2012, Cao et al. 2014, Altun et al. 2012). These heavy metal adsorbents have many advantages, such as a wide variety of raw materials, low cost, low monomer toxicity, simple synthesis process as well as environmental friendly. Some functional molecules including diethylenetriamine (Cao et al. 2014), citric acid (Altun et al. 2012), thiosemicarbazide (Liu and Gao 2016) have been used as modified monomers in past studies, but the limited number of functional groups introduced onto natural polymer, weaken the adsorption capacity and adsorption efficiency. Amino-terminated hyperbranched polymers (ATHBP) have unique molecular structures and properties such as the absence of chain entanglement, many nanopores, low viscosity and high solubility (Zhang 2009; Eissa et al. 2015). In addition, amino-terminated hyperbranched polymers have a large number of functional groups, which can be effective in the adsorption of heavy metal ions. The adsorption sites of agricultural and forestry wastes can be increased significantly by the modification of amino-terminated hyperbranched polymers. On the other hand, the remarkable structure of hyperbranched polymer such as the absence of chain entanglement can make many adsorption sites expose on the molecular surface, which achieves full adsorption of heavy metal ions.

Walnut shells (WNS) is an abundant agricultural residue with good stability, large specific surface area, high mechanical strength, good chemical stability and excellent regenerative abilities. Structural analyses as indicated approximately 17% cellulose, 36% hemicelluloses and 36% lignin, were made as described in past study (Li et al. 2004). Walnut shells contain many functional groups such as hydroxyl, aldehyde group, methoxyl and so on. In this paper, the amino-terminated hyperbranched polymer (ATHBP) modified walnut shell (FWNS) was prepared and the adsorption behavior for Pb(II) ions in aqueous solution was also investigated.

Experimental

Materials

Walnut shell (WNS) was collected from Qinhuangdao, China. Glycidyl methacrylate (GMA), HCl, $Pb(NO_3)_2$, the emulsifier(OP-10), $K_2S_2O_8$, 1,4-dioxane, sodium bisulfite were obtained from Tianjin Guangfu Technology Development Co., LTD (Tianjin, P. R. China). Hyperbranched Polyethylenimine (HPEI, 50% (wt) aqueous solution, $\overline{M_n} = 8000\ g/mol$) was obtained from Hangzhou Yajian Biotechnology Co., LTD (Hangzhou, P. R. China). All reagents were of analytic reagent grade and used without further purification.

Preparation of functional walnut Shell (FWNS)

Before modification, Walnut shells were boiled for 60 min and rinsed thoroughly with distilled water, and dried for more than 24 h at 110 °C. Then, the walnut shell was ground by a high-speed grinder until a powder of size smaller than 100 μm was obtained. The chemical modification of WNS was carried out as follows (Cao et al. 2014): Firstly, 4.0 g of WNS was putted into the solution with water containing an emulsifier (0.3 g) for 30 min at 40 °C. Then, 7.0 g GMA, 5.4 g $K_2S_2O_8$ and 3.6 g $NaHSO_3$ were added and the mixture was stirred using a constant temperature magnetic heater stirrer for 60 min at 15 °C. Finally, the resulting solid was washed with acetone and ethanol and dried to constant weight at 80 °C, WNS-g-GMA was obtained.

6.0 g HPEI and 1.0 g WNS-g-GMA were added to 50 mL mixed solution (V_{Water}: $V_{1,4\text{-dioxane}} = 1{:}3$) and stirred at constant temperature 85 °C for 30 h. The reaction mixture was filtered and extracted with deionized water for 48 h, and the solid was dried at 80 °C in vacuum for 3 h. FWNS was obtained. These chemical modifications are illustrated in Fig. 1.

Characterization methods

A Nicolet380 Spectrometer System (Nicolet Company, U.S.A.) was used for Fourier transform infrared (FTIR) analysis to confirm the presence of ATHBP on WNS.

The XRD measurement was taken by a Rigaku D-max-2550/PC diffractometer (Rigaku Inc., Tokyo, Japan). The XRD pattern was obtained using Cu Kα 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.

The zeta potential of FWNS at various acidities was measured by solid addition method (Kiefer et al. 1997).

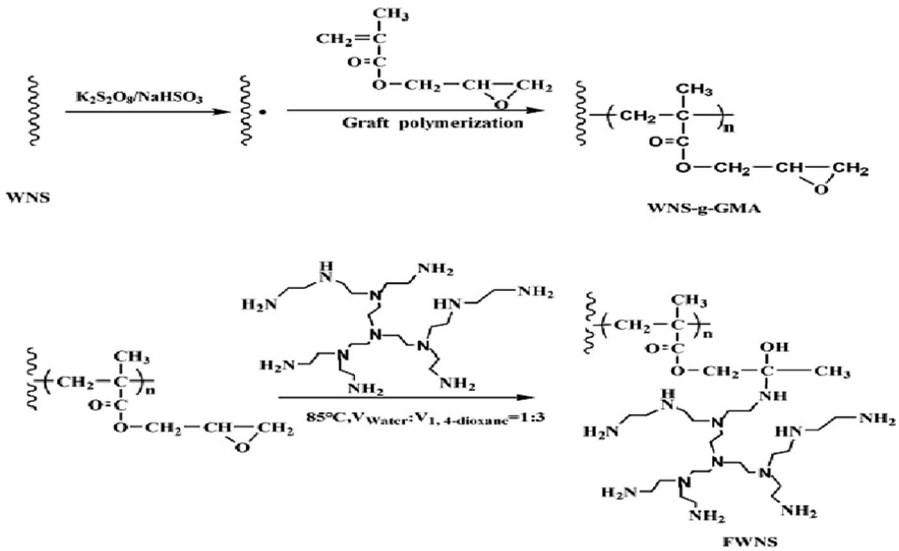

Fig. 1 Associated reactions of the modification process

Scanning electron microscopy(SEM) images were observed on a Hitachi S-3400 N scanning microscope (Hitachi, Japan). The WNS samples were suspended in a bottle with a small amount of ethanol using ultrasound. The sample was mounted on glass plates and the ethanol removed from the sample surface, followed by application of a thin coating of gold in a vacuum.

Adsorption experiment

The desired dose of FWNS was added to a series of 40 mL tube containing the desired concentration of $Pb(NO_3)_2$ in aqueous solution, and the adsorption experiments were then performed in a shaking bath. The effect of initial pH of the solution on the removal of Pb(II) ions was determined over the range of 2.0–6.0. The solution pH was adjusted with 0.1 M NaOH or 0.1 M HCl as appropriate. The influences of adsorbent doses (from 0.25 to 2.5 g L^{-1}) on removal of Pb(II) ions were also investigated. Additionally, the isothermal adsorption experiment were determined at different initial Pb(II) ions concentrations (50–700 mg/L) at pH = 6.0 and thermodynamic studies were investigated at different temperatures of 293 K, 303 K, 313 K, 323 and 333 K. Kinetics experiments were carried out at pH = 6.0 and 298 K. During the adsorption experiments, the tube with adsorbent and adsorbate were stirred at 200 rpm for 2.0 h in a water bath constant temperature oscillator (SHZ-82, Jintan jingbo Experimental Instrument Company, China). Afterwards, the residual adsorbate concentrations were measured by atomic absorption spectrometer (Z-2000, Hitachi Limited Company, Japan). All experiments were carried out with three replicates (Cao et al. 2014).

The adsorption capacity (Q) of FWNS and WNS were calculated from the following expressions:

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

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

Adsorption and desorption

In order to explore the recyclability of FWNS adsorbent, regeneration experiments were performed. The FWNS containing adsorbed Pb(II) was placed into 0.1 M HCl solution, and then was shaken at 20 °C for 2 h. Thereafter, the sorbent was removed from the solution and washed 3 times with deionized water. Five consecutive adsorption–desorption experiments were performed under the same conditions.

Results and discussion

FTIR analysis of FWNS

The FTIR spectrum of original WNS, WNS-g-GMA and FWNS are shown in Fig. 2. The peak located at 3400 cm^{-1} is assigned to the O–H stretching vibration of hydroxyl groups. The bands at around 2935 cm^{-1} are assigned to C–H stretching vibrations in methylene and methyl groups, and the peak at 1257 cm^{-1} can be assigned to C–O stretching vibrations in phenols, ether, or alcohols (Cao et al. 2014). Comparing the original WNS spectrum with that in Fig. 2b, the peak in the range of 1730 cm^{-1} can be attributed to the -C=O and the peak at 905 cm^{-1}, 846 cm^{-1} are assigned to epoxy group (Ding et al. 2014). The FTIR of FWNS is shown in Fig. 2c. The characteristic peak of epoxy groups at 905 cm^{-1}, 846 cm^{-1} is no longer evident, which suggests that opening ring reaction between the epoxy groups and amino-terminated hyperbranched polymer has occurred confirming that WNS-g-GMA has grafted with amino-terminated hyperbranched polymer.

XRD analysis of FWNS

XRD patterns of WNS (a), WNS-g-GMA (b) and FWNS(c) are shown in Fig. 3. The original WNS (Fig. 3a) shows scattering at 2θ = 22.08°, which are taken as peaks characteristic of WNS. The WNS-g-GMA (Fig. 3b) shows scattering at 2θ = 18.28°, 27.48°, 36.36°, which are taken as peaks characteristic of PGMA. The absence of the peak at 2θ = 18.28°, 27.48°, 36.36° in FWNS (Fig. 3c) shows that crystallinity has decreased, which indicates that HPEI grafted on WNS-g-GMA destroyed ordered structure of WNS-g-GMA.

SEM image analysis

The surface morphology of WNS, FWNS and FWNS- Pb(II) were observed with SEM (Fig. 4). The original WNS particles (Fig. 4a) show a smooth surface, while the surfaces of FWNS (Fig. 4b) are shown to be uneven, with more pores increasing the surface area and facilitating the adsorption of lead ions. The surface morphology of FWNS-Pb(II) (Fig. 4c) has a surface to form a thick sheet structure (Fig. 4c), which shows that Pb(II) ions are adsorbed on FWNS.

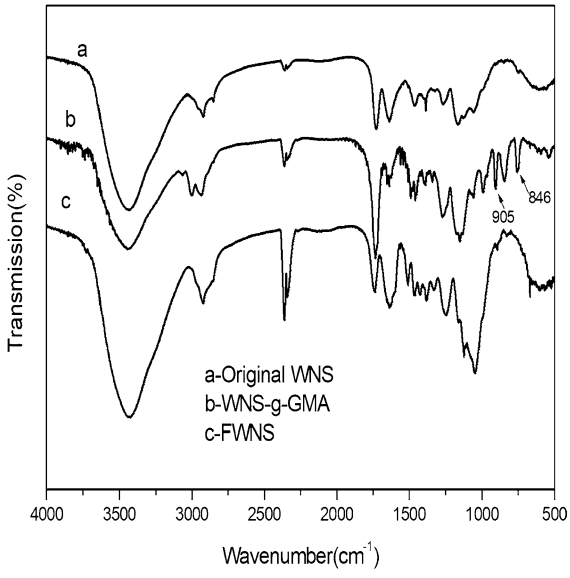

Fig. 2 FTIR spectrum of walnut shell (WNS) (**a**), WNS-g-GMA (**b**) and FWNS (**c**)

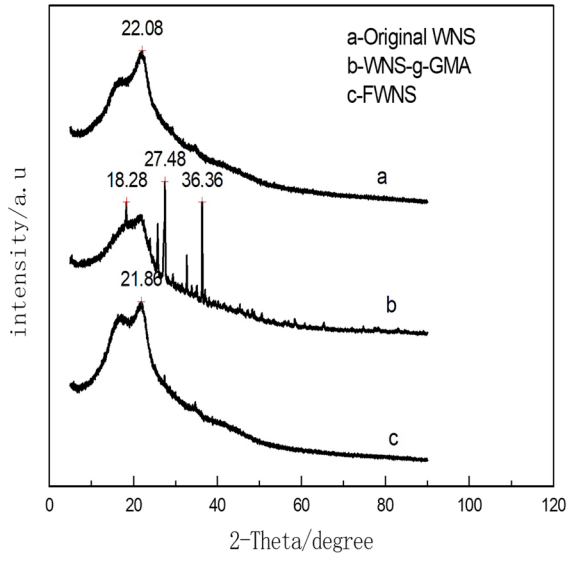

Fig. 3 XRD patterns of original walnut shell (WNS), WNS-g-GMA and FWNS

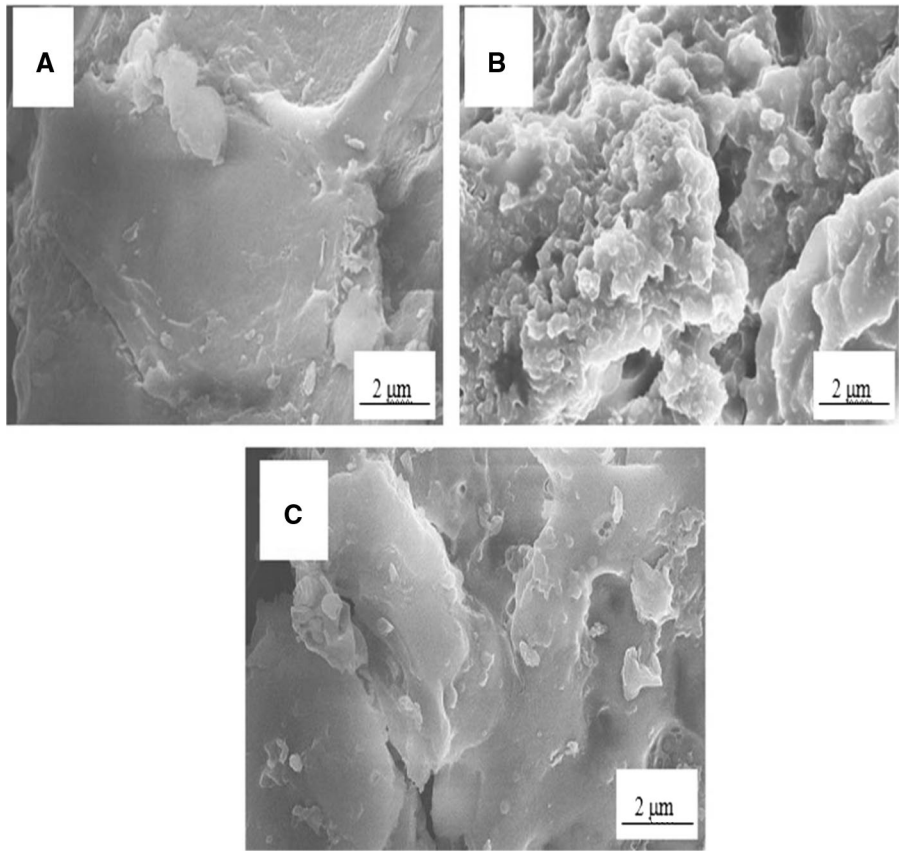

Fig. 4 SEM images of original walnut shell (WNS) (**a**), FWNS (**b**) and FWNS-Pb(II) (**c**)

Influence of pH

It is well known that the solution pH is the most important factor because of affecting the surface charge of adsorbents, the degree of ionization, and the speciation of adsorbates (Naghizadeh et al. 2011).

The influence of pH on Pb(II) ions adsorption and Zero-point charge of FWNS are shown in Fig. 5. There is a significant increase in lead ions adsorption capacity with pH from 2 to 6. It's probably because zeta potential varies in surface electric charge of the FWNS (Fig. 5B, pH_{pzc}≈8.62) (Cao et al. 2014; Kiefer

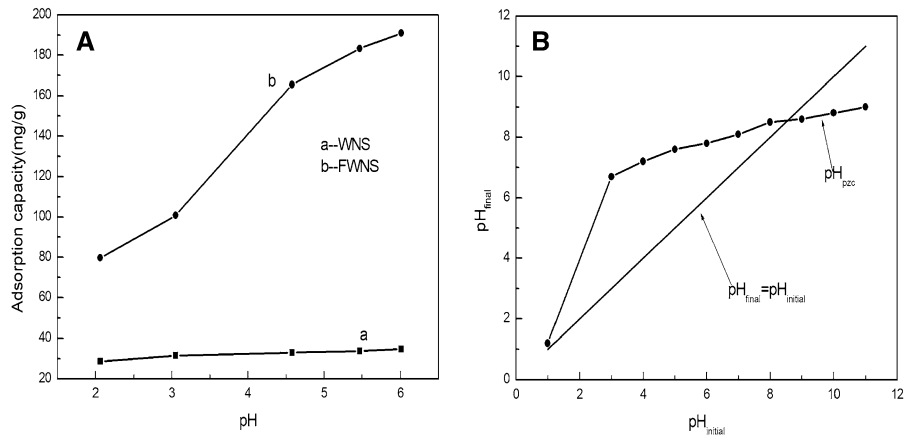

Fig. 5 The effects of pH on adsorption capacity **A** of Pb(II) ions by WNS and FWNS (conditions: temperature, 25 ± 1 °C, adsorbent dosage, 0.25 gL^{-1}, adsorption time, 120 min, initial Pb^{2+} concentration, 50.0 mg/L) and Zero-point charge of FWNS (**B**)

et al. 1997; Chen et al. 2010). The reduced metal uptake seen at low pH values may be attributed to the higher concentration of H^+ ions. More $–NH_3^+$ on the surface of FWNS, enhanced electrostatic repulsion between $–NH^{3+}$ with Pb(II) and chelation of $–NH_2$ groups with Pb(II) weakened (Mohammod et al. 2011). But, these results indicate that FWNS has higher adsorption capacity at lower pH value than other heavy metal adsorbents (Xie et al. 2011; Altun and Pehlivan 2012; Liu and Gao 2016). The adsorption capacity of FWNS towards Pb(II) ions reached about 190.96 mg/g at pH = 6.0. A possible explanation could be that amino-terminated hyperbranched polymers have a large number of adsorption sites, weaken the influence of pH on the adsorption capacity, and causing the adsorbent to have high adsorption capacity over a wider pH range.

At higher pH values, the lower H^+ concentration leads to more free $-NH_2$ groups in the system, which makes it easier to chelate with lead ions.

Influence of adsorbent dosage

The influence of the dosage of the original WNS and FWNS on adsorption capacity of Pb(II) ions is shown in Fig. 6. Using FWNS, When the dosage of adsorbent was gradually increased from 0.25 to 2.5 g L^{-1}, the capacity of adsorbent decreased sharply from 188.22 to 20.68 mg/g (Fig. 6). The possible reason for this is that the decrease in Pb(II) ions uptake at higher adsorbent dosage may be attributed to the competition of Pb(II) ions for available adsorption sites and an increase in the diffusion path length (Abdel et al. 2006). In addition, agglomeration of the adsorbent particles may also be the cause of the decrease of adsorption.

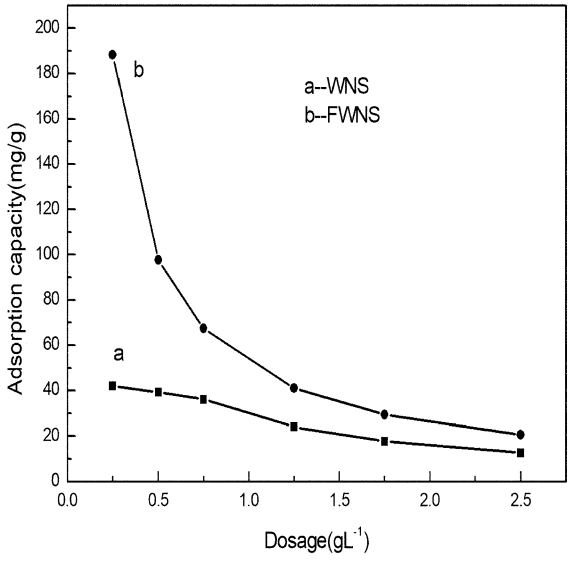

Fig. 6 The effects of adsorbent dosage on adsorption capacity of Pb(II) ions by WNS and FWNS (conditions: temperature, 25 ± 1 °C, pH = 6.0, react time, 120 min, initial Pb^{2+} concentration, 50.0 mg/L)

Adsorption isotherms

In this part, adsorption isotherms were investigated. The influence of initial Pb^{2+} concentration on Pb(II) ions adsorption by FWNS is shown in Fig. 7. Langmuir and Freundlich models were used (Ding et al. 2013; Parab and Sudersanan 2010). The relevant isotherm equations are listed as:

Langmuir isotherm:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad (1)$$

where Q_e (mg/g) is the corresponding adsorption capacity and C_e (mg/L) is the ultimate concentration of Pb(II) ions at equilibrium. Q_m (mg/g) is the theoretical maximum adsorption capacity of adsorbent

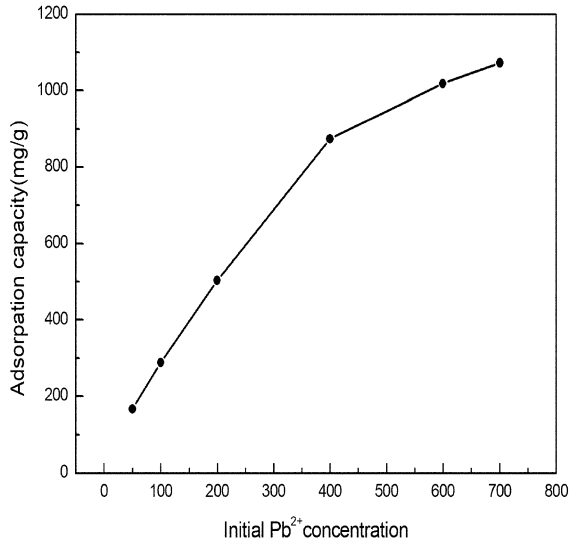

Fig. 7 Influence of initial Pb^{2+} concentration on Pb(II) ions adsorption by FWNS

for Pb(II) ions, and K_L (L/mg) is the Langmuir isotherm coefficient. A plot of C_e/Q_e versus C_e is shown in Fig. 8B, which shows that C_e/Q_e and C_e have a good linear relationship. The values of K_L and Q_m, obtained from Fig. 8B are listed in Table 1.

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. A plot of $\ln Q_e$ versus $\ln C_e$, is shown in Fig. 8A and the corresponding parameters are also listed in Table 1.

The results indicated the Langmuir model is a good fit for the equilibrium adsorption as indicated by the high values of R^2 (0.9939), and The calculated maximum adsorption capacity (Q_m) of FWNS for Pb(II) ions was 1250.00 mg/g, close to experiment value (1072.8 mg/g). The results of Langmuir model suggests that a homogeneous monolayer of Pb(II) ions was adsorbed onto FWNS particles (Cao et al. 2014; Yuvaraja et al. 2014). In addition, the adsorption of Pb(II) ions on FWNS was a dynamic chemisorption reaction, which depends on the adsorption affinity of the surface functional groups of.

FWNS and the bond energy (Cao et al. 2014; Feng et al. 2013). The adsorption capacity of FWNS is significantly larger than that of other modified natural polymers. The adsorption capacity of several modified natural polymers in the literature was listed in Table 2(Liu et al. 2013a, b; Cheng et al. 2021; Liu and Gao 2016; Liu et al. 2019). On the other hand, the remarkable structure of hyperbranched polymers and the absence of significant chain entanglements

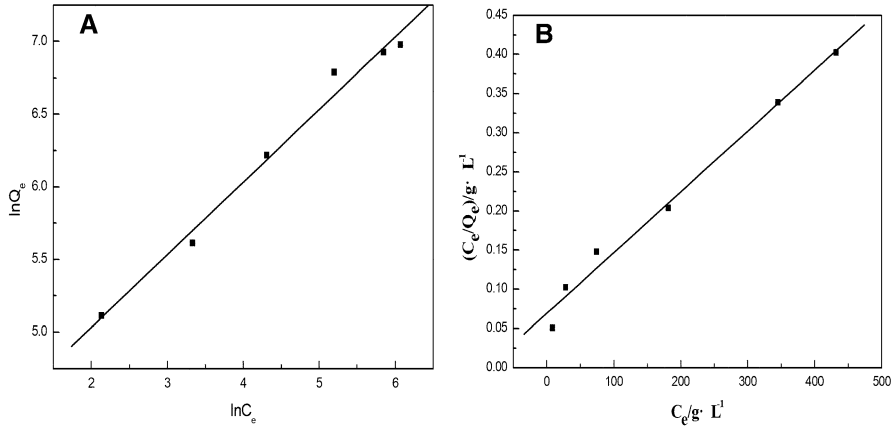

Fig. 8 Isotherm models for Pb(II) ions adsorption onto FWNS **A** Freundlich model, **B** Langmuir model

Table 1 Adsorption isotherm constants for Pb^{2+} adsorption onto the FWNS

*Experimental data

**Calculated data

Q_e*/mg/g	Langmuir			Freundlich		
	Q_m** /mg/g	K_L /L/mg	R^2	K_F	n	R^2
1072.8	1250.0	0.0117	0.9939	56.589	2.003	0.9758

Table 2 Adsorption capacity of several modified natural polymers for Pb^{2+}

Adsorbents	Adsorption capacity(mg/g)
Dithiocarbamate modified chitosan beads (Liu et al. 2013a, b)	359.68
1,3-diaminoguanidine monohydrochloride modified crofton weed (Cheng et al. 2021)	234.6
Aminothiourea modified walnut Shell (Liu and Gao 2016)	46.25
Triethylene tetramine modified walnut shell (Liu et al. 2019)	56.81
FWNS(in this paper)	1250

can increase the availability of surface adsorption sites.

A separation factor (R_L) to evaluate the suitability of an adsorption process, was defined as the following equation (Xia et al. 2011):

$$R_L = \frac{1}{1 + K_L C_0} \tag{3}$$

where C_0 (mg/L) is the initial Pb (II) ion concentration in solution and K_L(L/mg) is the Langmuir isotherm coefficient related to the free energy of adsorption. The values of R_L (0.1247–0.6309) at 298 K were in the range of 0–1, which implies that adsorption of Pb(II) ions on FWNS is a favorable uptake (Bhaumik et al. 2013).

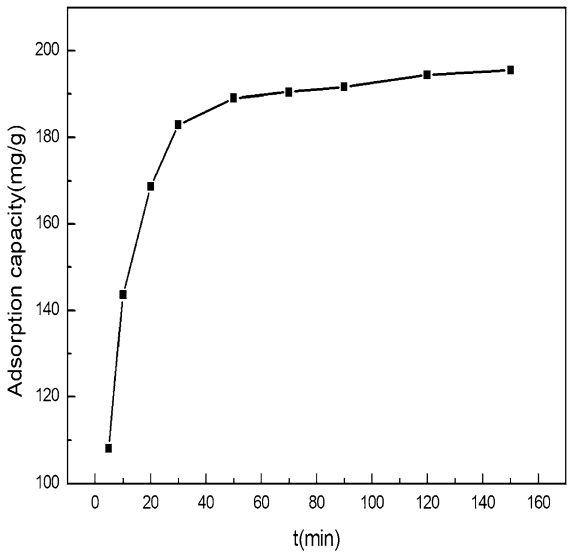

Fig. 9 Influence of time on Pb(II) ions adsorption by FWNS

Adsorption kinetics

In this section, In order to find out how rapidly the adsorption progress was and whether the adsorption process is controlled by chemical or physical adsorption, the adsorption dynamics were investigated (Chen et al. 2010). Figure 9 showed the influence of time on Pb(II) ions adsorption by FWNS.

Pseudo-first-order and pseudo-second-order diffusion models were used to discuss the relationship between adsorption capacity of adsorbate and adsorption time. The two equations are as follows:

Pseudo-first-order kinetic model:

$$\ln\left(Qe - Q_t\right) = \ln Qe - K_1 t \tag{4}$$

where Q_e (mg/g) and Q_t (mg/g) refer to the adsorption capacity of Pb(II) ions by FWNS at equilibrium and at time t (min), respectively. K_1 (1/min) is the equilibrium rate constant of pseudo-first-order adsorption.

Pseudo-second-order kinetic model:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} t \tag{5}$$

where K_2 (g/(mg/min)) is the equilibrium rate constant for pseudo-second-order adsorption. The applications of the models to the experimental data are shown in Fig. 10. The constants determined from the experimental data and correlation coefficients (R^2) are listed in Table 3.

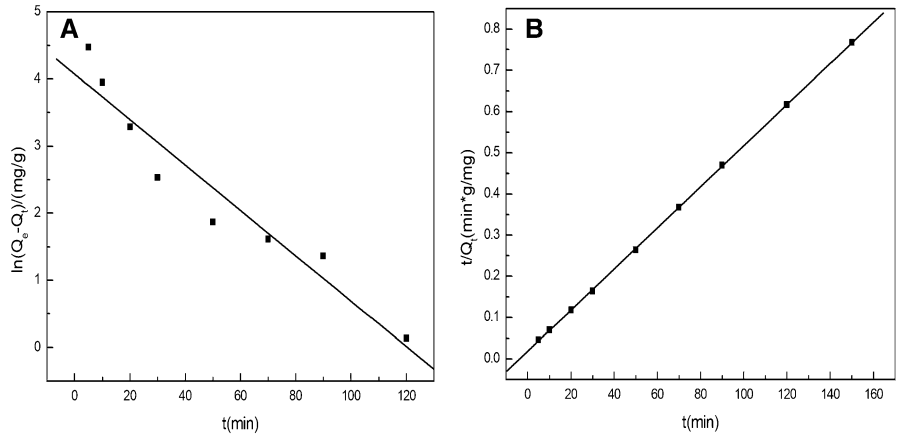

Fig. 10 Kinetic models for Pb(II) ions adsorption onto FWNS: **A** Pseudo-first-order kinetic plots **B** Pseudo-second-order kinetic plots

Table 3 Kinetic parameters for the adsorption of Pb^{2+} on FWNS with different models

Q_e^*/mg/g	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	k_1/min^{-1}	Q_e^{**}/mg/g	R^2	k_2/(g/mg/min)	Q_e^{**}/mg/g	R^2
195.53	0.034	58.72	0.9276	0.0014	200.00	0.9999

*Experimental data

**Calculated data

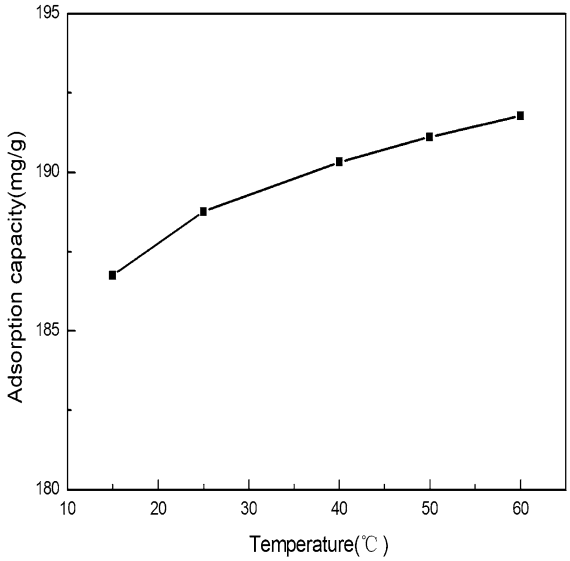

Fig. 11 Influence of temperature on Pb(II) ions adsorption by FWNS (conditions: adsorbent dosage, 0.25 gL^{-1}, pH = 6.0, adsorption time, 120 min, initial Pb^{2+} concentration, 50.0 mg/L)

The adsorption of Pb(II) ions on FWNS probably do not obey the pseudo-first-order kinetic model because obtained Q_e(58.72 mg/g) is quite different from the experiment value(195.53 mg/g) and the R^2 (0.9276) is low. By contrast, the results of pseudo-second-order equation are reasonable because of the high R^2 (0.9999) and good agreement with the calculated Q_e ($Q_{e,exp}$ = 195.53 mg/g). This result indicated that chemisorption was the rate-limiting step in adsorption process.

Thermodynamics of adsorption

The influence of temperature on the adsorption of Pb(II) ions on FWNS was investigated. Figure 11 showed the influence of temperature on Pb(II) ions adsorption by FWNS. ΔH and ΔS were obtained by the Eq. (6) (Lin et al. 2011):

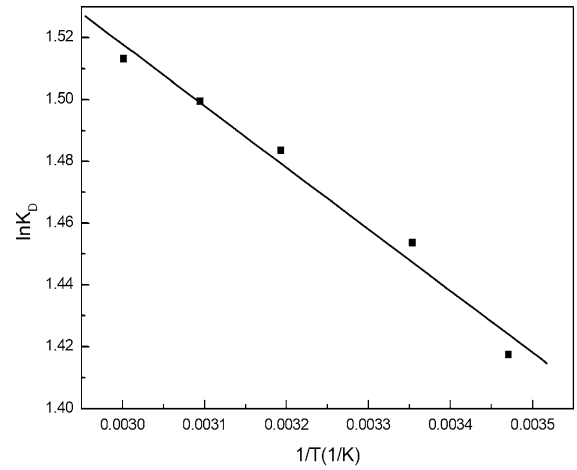

Fig. 12 $\log K_D \sim 1/T$ for FWNS

$$\ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{6}$$

where K_D (L/mol) is thermodynamic adsorption equilibrium constant and obtained by Eq. (7), and.

R is the gas constant valued 8.314 J/(mol K). Plots of $\ln K_D$ versus 1/T are shown in Fig. 12. The result shows $\ln K_D$ versus 1/T have a good linear relationship. The values of ΔH and ΔS, obtained from Fig. 12 are listed in Table 4.

$$K_D = \frac{Q_e}{C_e} \tag{7}$$

where Q_e is the equilibrium Pb(II) concentration on the adsorbent (mg/L) and C_e is the equilibrium Pb(II) concentration in solution (mg/L).

The Gibbs free energy of adsorption (ΔG) subsequently obtained by Eq. (8), are also listed in Table 4 (Gong et al. 2008).

Table 4 Thermodynamic parameters of adsorption of Pb^{2+} on FWNS

T(K)	ΔG(KJ·mol^{-1})	ΔH(KJ·mol^{-1})	ΔS(J·mol^{-1}·K^{-1})
293.15	−9.59	9.948	67.813
303.15	−10.27		
313.15	−11.29		
323.15	−11.97		
333.15	−12.64		

Table 5 Regeneration of FWNS

Desorption times	1	2	3	4	5
Removal efficiency/%	98.24	97.11	96.08	95.01	93.51

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

Seen from Table 4, ΔH value indicates the adsorption of Pb(II) ions on FWNS is endothermic. And the chelation between functional groups and Pb(II) ions on the surface of FWNS is also involved in the adsorption process. The higher the temperature is, the easier the adsorption is (Chen et al. 2010). The positive ΔS implied degrees of freedom of the liquid–solid interface increased during adsorption process of Pb(II) ions onto FWNS. Additionally, the adsorption reaction is a spontaneous nature because of negative values of ΔG. Furthermore, with the increase of temperature, the negative value of ΔG increases, which further proves that the temperature is favorable to the adsorption process.

Adsorption/desorption

In order to explore the possibility of recycling FWNS, the adsorption/desorption process was also explored. The efficiencies of removing lead ions from FWNS for five consecutive adsorption/desorption cycles are presented in Table 5. The results show the removal efficiency of lead ions from FWNS remains high, above 93%.

Conclusion

An efficient heavy metal adsorbent (FWNS) was prepared by grafting amino-terminated hyperbranched polymer onto walnut shell. Structural characterization using various instruments demonstrated that amino-terminated hyperbranched polymer was successfully grafted onto walnut shell. The results showed that FWNS had adsorption capacity over a wide pH range. The adsorption isotherms showed that the adsorption of Pb(II) ions on FWNS resulted in a homogeneous monolayer and was a dynamic chemisorption process. The adsorption behavior of Pb(II) ions is well described by the pseudo-second-order kinetic model. Furthermore, the adsorption process of Pb(II) ions by FWNS is spontaneous and endothermic. The higher temperature is favorable for the adsorption. The results demonstrated that FWNS can be reused. Finally, FWNS can be obtained from an agricultural byproduct, walnut shell, through a simple modification process at low cost, making it a competitive adsorption material in practice.

Acknowledgments This work was financially supported by S & T Program of Hebei (Grant no. 21323602D), Science and Technology Research and Development Program of Qinhuangdao (Grant no. 202005A057) and the Breeding Research Subjects of Yanshan University (Grant no.16LGY020). We are thankful to Dr. Rudolph Winter, professor at Department of Chemistry&Biochemistry, University of Missouri- St Louis who made modification in English.

Author contributions The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding The authors have not disclosed any funding.

Declarations

Conflict of interest The authors have not disclosed any competing interests.

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