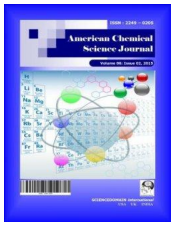

American Chemical Science Journal
12(4): 1-9, 2016, Article no.ACSJ.23548
ISSN: 2249-0205

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Removal of Pb(II) from Aqueous Solution by Acrylic Acid Modified Walnut Shell: Isotherms and Kinetics

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Authors' contributions

This work was carried out in collaboration between all authors. Author LC designed the study, performed the analytical studies and wrote the first draft of the manuscript. Author WX managed the analyses of the study. Author ZZ revised the manuscript. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/ACSJ/2016/23548
Editor(s):
(1) Anonymous.
Reviewers:
(1) Anonymous, Jawaharlal Nehru Technological University, Anantapur, India.
(2) Yijun Tang, University of Wisconsin Oshkosh, USA.
(3) P. N. Palanisamy, Kongu Engineering College, Tamil Nadu, India.
Complete Peer review History: http://sciencedomain.org/review-history/13036

Original Research Article

Received 7th December 2015
Accepted 5th January 2016
Published 21st January 2016

ABSTRACT

The adsorption isotherms and kinetics of acrylic acid modified walnut shell (AA-WNS) for Pb(II) were investigated in the temperature range of 288-308K. Scanning electron microscope (SEM) was utilized for evaluation of the developed walnut shell. Adsorption isotherm data were better interpreted by Langmuir isotherm model, and the maximal adsorption capacity was 238.65 mg g^{-1} at 308 K. The adsorption kinetic data were well correlated by pseudo-second-order model. The adsorption process was governed by both film and intraparticle diffusion, with film diffusion at the fast stage followed by intraparticle diffusion. A Boyd kinetic plot confirms that the slowest step of Pb(II) adsorption by AA-WNS is film diffusion. The thermodynamic parameters ΔG, ΔH and ΔS were determined. Recycling properties of AA-WNS were studied, indicating that it can be reused for Pb(II) adsorption.

Keywords: Adsorption; lead ions; acrylic acid; walnut shell; isotherms; kinetics.

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1. INTRODUCTION

Water pollution caused by heavy metals has been of great concern due to its toxicity and non-biodegradability. As a frequently-used heavy metal ion, lead can be assimilated and stored in living organisms, causing deleterious effects on the nervus, brain, kidney, cardiovascular and other vital organs [1,2]. Hence, various techniques for Pb(II) removal have been developed, such as precipitation, ion-exchange, electrochemical, and adsorption [3-5]. Among them, adsorption is a widely applied technique [6]. In particular, biosorption is a promising ecofriendly technique due to its low-initial cost, environmental benign, regeneration, and availability of biomass [7,8]. Recently, a wide of the efficient adsorbents from agricultural residues have been used for Pb(II) removal from wastewater including *Imperata cylindrica* leaf powder [9], cotton [10], *Pinus sylvestris* [11], Nipah palm shoot [12], *Azolla filiculoides* [13], sugarcane bagasse [14], peanut husk [15], *Rosa centifolia* petals [16], banana stem [17], spent grain [18], etc.

Walnut (*Juglans regia*), the fruit of walnut trees, belongs to Juglandaceae. According to FAOSTAT, the major producers of walnuts include China, Iran, United States, Turkey, Mexico, Ukraine, India, Chile, France and Romania, and a total of 3.4×10^6 tonnes of walnuts were produced in 2013 [19]. Walnut shell (WNS) makes up about 30 - 50% of walnut fruit, and it is an abundant agricultural waste in China with high mechanical strength, non-toxicity, well-functionalized surface property, chemical inertness, easy regeneration and biodegradability. Thus, it can be made into activated carbon, and the ground WNS can be used for the cleaning of aviation parts. Moreover, it could be used for removing metal ions such as Cr(VI) [20], Cu(II) [21], Pb(II), Cd(II) and Ni(II) [22]. However, raw WNS has low metal removal and slow process kinetics. The adsorption capacity of WNS could be enhanced by chemical modification. For example, the citric acid treated WNS was used for Cr(VI) removal, and its adsorption capacity was 0.596 mmol L^{-1} which is nearly four times than that of raw WNS [23]. However, studies on WNS modification for the removal of metal ions are still insufficient, especially for Pb(II) removal.

The objective of this work is to explore a new economic method for WNS utilization and to improve the treatment capability for wastewater containing lead ions. Thus, acrylic acid modified walnut shell (AA-WNS) was synthesized and used for Pb(II) removal. Adsorption isotherms, kinetics and mechanism of Pb(II) adsorption on AA-WNS were discussed. Moreover, the reusability of AA-WNS was studied.

2. EXPERIMENTAL

2.1 Reagents and Instruments

Acrylic acid (AA), acetone, and n-hexane were obtained from Shanghai Chemical Reagent Co. Ltd (China) and used as received. HNO_3 (98%), NaOH, HCl (35%) and $KMnO_4$ were supplied by Shanghai Lingfeng Chemical Reagent Co. Ltd. $Pb(NO_3)_2$ was supplied by Sinopharm Chemical Reagent Co. Ltd. All the chemicals were analytical grade. The surface morphology of the samples was performed on a TM3030 scanning electron microscope (SEM) (Hitachi, Japan).

2.2 AA-WNS Preparation

WNS obtained from Xinjiang (China) was crushed and sieved to select the particles with diameter between 500 μm and 1000 μm. The sample was washed with water until the water became clear, and then dried to a constant weight. The clean WNS (30 g) was immersed in NaOH solution (1 mol L^{-1}) for 24 h, and dried at 90°C for 48h after being washed to neutral. The grafting process of AA was carried out by the method reported in the literature [24]. In brief, the treated WNS (15 g) was preactivated with 250 mL $KMnO_4$ solution (0.016 mol L^{-1}) at 25°C for 30 min followed by filtration and washing, and then the grafting reaction was carried out by dispersing the above product in 250 mL AA/n-hexane solution with 0.825 mol L^{-1} AA at 69°C for 1.5 h. The mixture was treated with 100 mL acetone for 10 h to remove the homopolymer followed by filtration, and then washed with hot deionized water and acetone, respectively. Finally, the product (AA-WNS) was obtained by drying.

2.3 Graft Yield (*GY*) Determination

The graft yield of AA-WNS was determined by soaking AA-WNS (1 g) into 100 mL NaOH solution (0.01 mol L^{-1}) for 24 h. Then, three aliquots (25 mL) of the residual solution were back-titrated with hydrochloric acid solution (0.01mol L^{-1}). The graft yield can be expressed as follows

$$GY(\%) = \frac{(C_{NaOH}V_{NaOH} - 4\times C_{HCl}V_{HCl})}{w}\times M_{AA}\times 100 \quad (1)$$

where w (g) is the mass of AA-WNS, M_{AA} is the molecular weight of AA, V_{NaOH} (L) and V_{HCl} (L) are the volume of NaOH and HCl, and C_{NaOH} (mol L^{-1}) and C_{HCl} (mol L^{-1}) are the concentration of NaOH and HCl, respectively. The graft yield of AA-WNS is 17.73%.

2.4 Adsorption Experiments

Static adsorption experiments of Pb(II) on AA-WNS were conducted to study the isotherms, kinetics and mechanism. In the adsorption equilibrium tests, 25 mL Pb(II) solutions (pH = 5.0) with different initial concentrations (0.3-6.0 mmol L^{-1}) were mixed with 45 mg AA-WNS at different temperatures. After equilibrium, the residual Pb(II) concentration in solution was analyzed by centrifuging and then measuring with ethylene diamine tetra acetic acid disodium salt (EDTA) using xylenol orange as indicator. The adsorption capacity of Pb(II), q_e (mg g^{-1}), was estimated by

$$q_e = \frac{(C_0 - Ce)V}{w} \quad (2)$$

where C_0 (mg L^{-1}) and C_e (mg L^{-1}) are Pb(II) concentration at initial and at equilibrium, w (g) is the mass of AA-WNS, and V (L) is metal ion solution volume.

According to the above method, the adsorption capacity of WNS was determined in 25 mL 5.0 mmol L^{-1} Pb(II) solution at 298K and it is 11.08 mg g^{-1}.

The adsorption kinetics were determined by placing 45 mg AA-WNS in 25 mL 5 mmol L^{-1} Pb(II) solution (pH=5.0) at a constant temperature (288, 298 or 308K). At predetermined time, the residual Pb(II) concentration in solution was measured by titration with EDTA using xylenol orange as indicator. The amount of Pb(II) adsorbed onto AA-WNS at time t, q_t (mg g^{-1}), was calculated as follows:

$$q_t = \frac{(C_0 - C_t)V}{w} \quad (3)$$

where C_t (mg L^{-1}) is Pb(II) concentration at time t. All the tests were performed for three times and the mean values were reported.

2.5 Desorption and Regeneration

To regenerate the used AA-WNS, Pb(II)-loaded AA-WNS (45 mg) was treated with 20 mL HNO_3 solution (1 mol L^{-1}) at 25°C for 24 h. Then the regenerated adsorbent was filtered, washed and dried for the adsorption-desorption tests. Adsorption percentage for each cycle is equal to the ratio of the adsorption amount of regenerate adsorbent for Pb(II) to that of fresh adsorbent.

3. RESULTS AND DISCUSSION

3.1 SEM Analysis

Fig. 1 shows the SEM images of WNS and AA-WNS. From Fig. 1, there appeared rougher texture and more irregular porous on the surface of AA-WNS compared with WNS, indicating AA-WNS is favorable for Pb(II) adsorption.

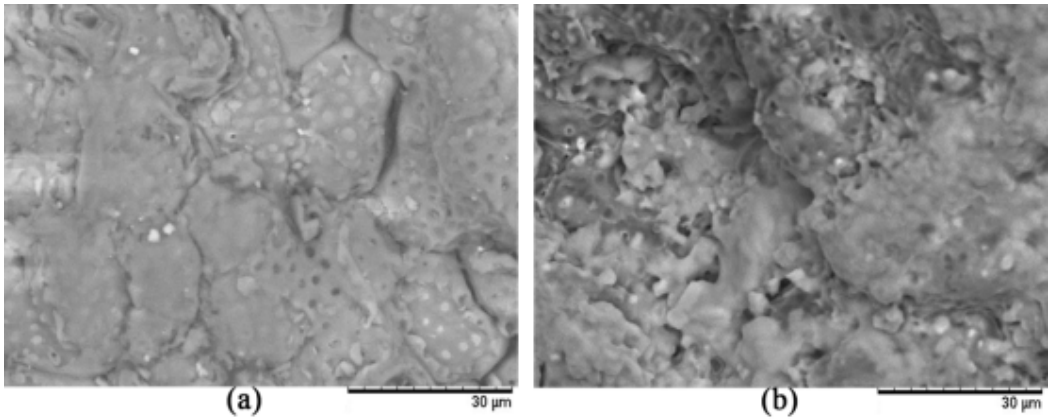

Fig. 1. SEM images of (a) WNS and (b) AA-WNS

3.2 Adsorption Isotherms

The isotherm for the removal of Pb(II) by AA-WNS at 288-308 K was shown in Fig. 2. From Fig. 2, the adsorption capacity of AA-WNS increased with the increase in temperature, suggesting the endothermic nature of Pb(II) adsorption onto AA-WNS. At a fixed temperature, the adsorption capacity increases with the increase of Pb(II) concentration.

In this work, Langmuir [25] and Freundlich [26] models were selected to fit the equilibrium data, and they were expressed as

$$\text{Langmuir isotherm: } q_e = \frac{C_e q_m K_L}{1 + C_e K_L} \quad (4)$$

$$\text{Freundlich isotherm: } q_e = K_F C_e^{1/n} \quad (5)$$

where q_m (mg g^{-1}) is the adsorption capacity of saturation, K_L is Langmuir constant, and K_F and n are Freundlich constants reflecting adsorption capacity and adsorption intensity, respectively.

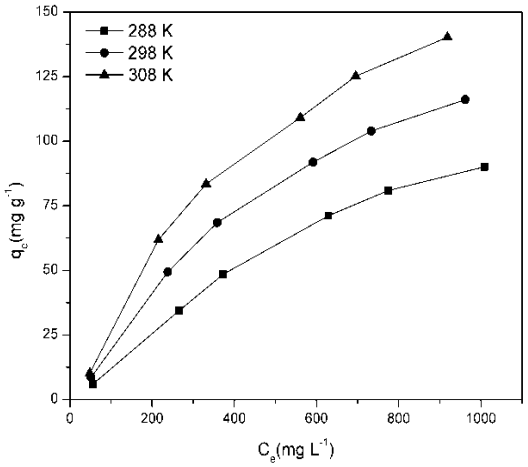

Fig. 2. Adsorption isotherms of AA-WNS for Pb(II) at different temperatures

The adsorption isotherm parameters were shown in Table 1. By comparing correlation coefficient, the adsorption of Pb(II) onto AA-WNS obeys Langmuir isotherm model and the process is a monolayer adsorption. The values of K_L are positive, indicating it is a favorable adsorption [27]. Favorability of adsorption can be further predicted using the separation factor (R_L) defined as $R_L = 1/(1+K_L C_0)$. If $R_L > 1$, unfavorable; $R_L = 1$, linear; $0 < R_L < 1$, favorable; $R_L = 0$, irreversible. The R_L values were in range of 0-1, implying that Pb(II) was adsorbed favorably by AA-WNS.

On the other hand, the theoretical maximum adsorption capacity (q_{max}) can be calculated by the value of GY as follows

$$q_{\max} = GY \times M_{Pb} / M_{AA} \quad (6)$$

where M_{Pb} and M_{AA} are the molecular weight of Pb(II) and AA. Based on Eq. (6), when GY=17.73 %, q_{max} is 255.12 mg g^{-1} which is larger than those (204.15-238.65 mg g^{-1}) obtained by Langmuir isotherm, indicating that only a part of functional groups of AA-WNS works.

The comparison of maximum adsorption capacity of various adsorbents for Pb(II) was listed in Table 2. From Table 2, the AA-WNS used in this work has larger adsorption capacity.

3.3 Adsorption Kinetics

The effect of contact time on Pb(II) adsorption was shown in Fig. 3. From Fig. 3, the adsorption process of AA-WNS for Pb(II) involves three stages: Fast, slow and equilibrium. In the fast stage (0-120 min), the AA-WNS surface is vacant and adsorption is controlled by the diffusion process. While in the slow stage (120-480 min), Pb(II) uptake is limited due to insufficiency of available adsorption sites. Fig. 3 also illustrated that a high temperature is favorable to Pb(II) uptake.

Table 1. Adsorption isotherm constants for Pb(II) adsorption onto AA-WNS

T (K)	Langmuir				Freundlich		
	K_L (L mg^{-1})	q_m (mg g^{-1})	R_L	R^2	K_F (mg g^{-1})/(g L^{-1})$^{1/n}$	n	R^2
288	0.0082	204.15	0.647-0.094	0.9938	0.6420	1.3850	0.9791
298	0.0128	212.54	0.540-0.063	0.9960	1.4097	1.5416	0.9755
308	0.0156	238.65	0.491-0.052	0.9938	2.0751	1.6041	0.9715

Table 2. Comparison of adsorption capacity of Pb(II) onto various adsorbents

Adsorbents	q_m mg g^{-1}	Modifying agent(s)	References
Walnut shell	238.65	Acrylic acid	This work
Walnut shell	11.08		This work
Imperata cylindrica leaf powder	13.5	Sodium hydroxide	[9]
Cotton	28.67	Thioglycolic acid	[10]
Pinus sylvestris	22.22	Formaldehyde in Sulfuric acid	[11]
Nipah palm shoot	52.86	Mercaptoacetic acid	[12]
Azolla filiculoides	228	Hydrogen eroxide-Magnesium	[13]
Sugarcane bagasse	189	Succinic anhydride and $NaHCO_3$ solution	[14]
	313	Succinic anhydride, and Triethylenetetramine	
	189	Succinic anhydride and Ethylenediamine	
Peanut husk	29.14	Formalin	[15]
Rosa centifolia petals	135.14	Sodium hydroxide	[16]
Banana stem	91.74	Formaldehyde	[17]
Spent grain	35.5	Sodium hydroxide	[18]

To analyze the adsorption rate of Pb(II) onto AA-WNS, the pseudo-first-order, pseudo-second-order [28] and Elovich [29] models were used to fit the adsorption data. They are expressed respectively as

Pseudo-first-order model: $$q_t = q_e(1-e^{-k_1 t}) \quad (7)$$

Pseudo-second-order model: $$q_t = \frac{k_2 q_e^2 t}{1+k_2 q_e t} \quad (8)$$

Elovich model: $$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad (9)$$

where k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the adsorption rate constants of pseudo-first-order and pseudo-second-order model, respectively. α (mg g^{-1} min^{-1}) is the initial adsorption rate, and β (g mg^{-1}) is the desorption constant.

The parameters obtained from the fits of these kinetic models were listed in Table 3. From Table 3, the adsorption process of Pb(II) onto AA-WNS obeys pseudo-second-order model due to the higher correlation coefficient (R^2>0.9883). The increasing of k_2 values with temperature indicated the adsorption of Pb(II) onto AA-WNS is endothermic [27,30]. Besides, Elovich model also fitted the experimental data well, indicating the Pb(II) adsorption onto AA-WNS is not only chemisorption, but also an ion exchange reaction [29].

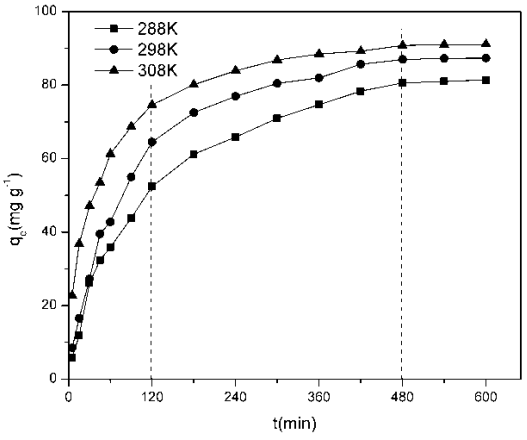

Fig. 3. Adsorption kinetics of Pb(II) on AA-WNS at different temperatures

3.4 Controlling Step

In order to obtain the information of diffusion mechanism, the adsorption data were fitted by intraparticle diffusion model [6,31].

$$q_t = k_{id} t^{0.5} + C \quad (10)$$

where k_{id} (mg g^{-1} min$^{-0.5}$) is intraparticle diffusion rate constant. The plots of q_t against $t^{0.5}$ were shown in Fig. 4. From Fig. 4, the plots are multi-linear, suggesting the adsorption rate is limited by more than one diffusion mechanism [26,30]: Film diffusion and intraparticle diffusion. The initial portion of the plot indicated Pb(II)

Table 3. Kinetic parameters for Pb(II) adsorption onto AA-WNS

T (K)	$q_{e,exp}$ (mgg^{-1})	Pseudo-first-order			Pseudo-second-order			Elovich		
		k_1 (min^{-1})	$q_{e,cal}$ (mgg^{-1})	R^2	$k_2\times10^3$ (gmg^{-1} min^{-1})	$q_{e,cal}$ (mgg^{-1})	R^2	α (mgg^{-1} s^{-1})	β (gmg^{-1})	R^2
288	81.02	0.0095	78.78	0.9827	0.1107	94.70	0.9963	2.907	0.0558	0.9787
298	87.21	0.0120	85.03	0.9913	0.1395	99.55	0.9971	3.873	0.0528	0.9760
308	90.99	0.0232	86.83	0.9377	0.3567	94.91	0.9883	12.28	0.0643	0.9833

adsorption onto AA-WNS is effected by boundary layer, and the second portion indicated the intraparticle diffusion effect. The last portion is the equilibrium stage.

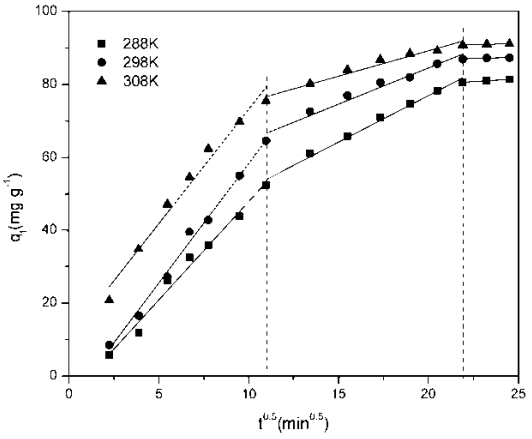

Fig. 4. Plots of q_t versus $t^{0.5}$ for Pb(II) adsorption onto AA-WNS

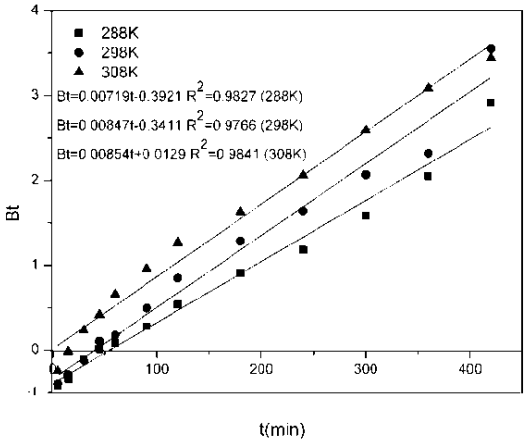

Fig. 5. Plots of Bt versus t for Pb(II) adsorption onto AA-WNS

The actual control step of Pb(II) adsorption onto AA-WNS was further investigated using Boyd equation [32].

$$Bt = -0.4977 - \ln(1-F) \tag{11}$$

With

$$F = \frac{q_t}{q_e} \tag{12}$$

where F is the fraction of Pb(II) adsorbed at time t. The values of Bt and F at each time t can be obtained from Eq.(11) and (12). If the plots of Bt against time t are linear passing through the origin, the intraparticle diffusion is the rate-controlling step, or otherwise film diffusion is the rate-controlling step [31]. As shown in Fig. 5, the line Bt versus t did not pass through the origin, indicating the process for Pb(II) adsorption by AA-WNS is dominated by the film diffusion.

3.5 Thermodynamic Parameters

Thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were obtained using the following equations [3,23,31]

$$K_c = \frac{C_{e,s}}{C_e} \tag{13}$$

$$\Delta G = -RT\ln K_c \tag{14}$$

$$\log K_c = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \tag{15}$$

where $C_{e,s}$ (mg L^{-1}) is the solid phase concentration at equilibrium. K_c is the equilibrium distribution coefficient. R (8.314 J mol^{-1} K^{-1}) is the gas constant, and T is the temperature in kelvins. The values of ΔH and ΔS were obtained from the slope and intercept of the linear plot of ln$K$c versus 1/T, and the thermodynamic parameters were listed in Table 4. From Table 4, the negative ΔG indicated the Pb(II) adsorption process by AA-WNS is a spontaneous.

Table 4. Thermodynamic parameters of Pb(II) adsorption onto AA-WNS

	ΔG (kJ mol^{-1})		ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
288 K	298 K	308 K		
-9.12	-9.65	-10.11	5.05	49.25

The positive ΔH indicated that the adsorption of Pb(II) by AA-WNS is endothermic, suggesting a higher temperature is favorable for Pb(II) adsorption. The positive ΔS suggested an increase in randomness at the solid/solution interface during the Pb(II) adsorption.

3.6 Recycling Properties of AA-WNS

To evaluate the regeneration capability of AA-WNS, the recovery tests were conducted and the results were listed in Table 5. From Table 5, the recovered AA-WNS does not show significant decrease in efficacy, maintaining high removal efficiency of 89.82% for Pb(II) despite four cycles. Thus, the adsorbent can be reused in Pb(II) removal.

Table 5. The regeneration capacity of AA-WNS

Cycle number	I	II	III	IV
q (mg g^{-1})	81.45	79.50	78.67	78.33
Adsorption percentage (%)	93.40	91.16	90.21	89. 82

4. CONCLUSION

In this work, AA-WNS was prepared and used as an effective adsorbent to improve Pb(II) adsorption process. The samples of WNS and AA-WNS were characterized by SEM analysis. The adsorption data are well interpreted by Langmuir model, and the maximum adsorption capacity for Pb(II) is 204.15, 212.54 and 238.65 mg g^{-1} at 288, 298 and 308 K, which is less than the theoretical maximum adsorption capacity (q_{max}), suggesting that only a part of functional groups works. The pseudo-second-order model can well describe the adsorption kinetics of Pb(II) onto AA-WNS and the adsorption process was governed by both film and intraparticle diffusion. A Boyd kinetic plot suggested that the controlling step of Pb(II) adsorption by AA-WNS is film diffusion. The values of ΔG, ΔH and ΔS for Pb(II) adsorption process suggested the process is spontaneous, endothermic and an increase in randomness. Moreover, the recovered AA-WNS maintained high removal efficiency of 89.61% for Pb(II) despite four cycles. Based on the research results, AA-WNS is an effective low-cost adsorbent for Pb(II) removal from aqueous solution.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Tao YF, Qiu Y, Fang SY, Liu ZY, Wang Y, Zhu JH. Trapping the lead ion in multi-components aqueous solution by natural clinoptilolite. Journal of Hazardous Materials. 2010;180:282–288.
2. Guo H, Ren YZ, Sun XL, Xu YD, Li XM, Zhang TC, et al. Removal of Pb^{2+} from aqueous solutions by a high-efficiency resin. Applied Surface Science. 2013;283:660–667.
3. Liu W, Yin P, Liu XG, Dong XQ, Zhang J, Xu Q. Thermodynamics, kinetics and isotherms studies for gold(III) adsorption using silica functionalized by diethylenetriaminemethylenephosphonic acid. Chemical Engineering Research and Design. 2013;91:2748–2758.
4. Wong KK, Lee CK, Low KS, Haron MJ. Removal of Cu and Pb from electroplating wastewater using tartaric acid modified rice husk. Process Biochemisty. 2003;39:437–445.
5. Liu CK, Bai RB, Ly QS. Selective removal of copper and lead ions by diethylenetriamine-functionalized adsorbent: Behaviors and mechanisms. Water Research. 2008;42:1511–1522.
6. Liu Y, Kang YR, Huang DJ, Wang AQ. Cu^{2+} removal from aqueous solution by modified chitosan hydrogels. Journal of Chemical Technology and Biotechnology. 2012;87:1010–1016.
7. Deniz F. effective removal of maxilon red GRL from aqueous solutions by walnut shell: Nonlinear kinetic and equilibrium models. Environmental Progress and Sustainable Energy. 2014;33:396–401.
8. Gadd GM. Biosorption: Critical review of scientific rationale, environmental

importance and significance for pollution treatment. Journal of Chemical Technology and Biotechnology. 2009;84:13–28.
9. Hanafiah MAK, Ibrahim SC, Yahya MZA. Equilibrium adsorption study of lead ions onto sodium hydroxide modified Lalang (*Imperata cylindrica*) leaf powder. Journal of Applied Sciences Research. 2006;2:1169–1174.
10. Wu Z, Cheng Z, Wei M. Adsorption of Pb(II) from glucose solution on thiol-functionalized cellulosic biomass. Bioresource Technology. 2012;104(1):807-809.
11. Taty-Costodes VC, Fauduet H, Porte C. Removal of Cd(II) and Pb(II) ions from aqueous solutions by adsorption onto sawdust of *Pinus sylvestris.* Journal of Hazardous Materials B. 2003;105:121–142.
12. Wankasi D, Horsfall Jr, Spiff AI. Sorption kinetics of Pb^{2+} and Cu^{2+} ions from aqueous solution by Nipah palm (*Nypa fruticans* Wurmb) shoot biomass. Electronic Journal of Biotechnology. 2006;9:587–592.
13. Ganji MT, Khosravi M, Rakhsaee R. Biosorption of Pb, Cd, Cu and Zn from wastewater by treated *Azolla filiculoides* with H_2O_2/$MgCl_2$. International Journal of Environmental Science and Technology. 2005;1:265–271.
14. Karnitz Júnior O, Gurgel LVA, Perin de Melo JC, Botaro VR, Melo TMS, Gil RPF, et al. Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse. Bioresource Technology. 2007;98:1291–1297.
15. Li Q, Zhai J, Zhang W. Kinetic studies of adsorption of Pb(II), Cr(III) and Cu(II) from aqueous solution by sawdust and modified peanut husk. Journal of Hazardous Materials B. 2006;141:163–167.
16. Nasir MH, Nadeem R, Akhtar K, Hanif MA, Khalid AM. Efficacy of modified distillation sludge of rose (*Rosa centifolia)* petals for lead(II) and zinc(II) removal from aqueous solutions. Journal of Hazardous Materials. 2007;147:1006–1014.
17. Noeline BF, Manohar DM, Anirudhan TS. Kinetic and equilibrium modeling of lead(II) sorption from water and wastewater by polymerized banana stem in a batch reactor. Separation and Purification Technology. 2005;45:131–140.
18. Low KS, Lee CK, Liew SC. Sorption of cadmium and lead from aqueous solutions by spent grain. Process Biochemistry. 2000;36:59–64.
19. FAOSTAT. Available:http://faostat.fao.org (Accessed in Decemder 2015)
20. Pehlivan E, Altun T. Biosorption of chromium (VI) ion from aqueous solutions using walnut, hazelnut and almond shell. Journal of Hazardous Materials. 2008;155:378–384.
21. Wang XS, Li ZZ, Sun C. A comparative study of removal of Cu(II) from aqueous solutions by locally low-cost materials: Marine macroalgae and agricultural by-products. Desalination. 2009;235:146–159.
22. Bulut Y, Tez Z. Removal of heavy metals from aqueous solution by sawdust adsorption. Journal of Environmental Sciences. 2007;19:160–166.
23. Altun T, Pehlivan E. Removal of Cr(VI) from aqueous solutions by modified walnut shells. Food Chemistry. 2012;132:693–700.
24. Geay M, Narchetti V, Clément A, Looubinoux B, Gérardin P. Decontamination of synthetic solutions containing heavy metals using chemically modified sawdusts bearing polyacrylic acid chains. Journal of Wood Science. 2000; 46:31–333.
25. Ding DH, Zhao YX, Yang SJ, Shi WS, Zhang ZY, Lei ZF, et al. Adsorption of cesium from aqueous solution using agricultural residue-Walnut shell: Equilibrium, kinetic and thermodynamic modeling studies. Water Research. 2013;47:2563-2571.
26. Gao ZP, Yu ZF, Yue TL, Quek SY. Adsorption isotherm, thermodynamics and kinetics studies of polyphenols separation from kiwifruit juice using adsorbent resin. Journal of Food Engineering. 2013; 116:195–201.
27. Yang JB, Yu MQ, Qiu T. Adsorption thermodynamics and kinetics of Cr(VI) on KIP210 resin. Journal of Industrial and Engineering Chemistry. 2014;20:480–486.
28. Liu LH, Lin Y, Liu YY, Zhu H, He Q. Removal of methylene blue from aqueous solutions by sewage sludge based granular activated carbon: Adsorption equilibrium, kinetics and thermodynamics. Journal of Chemical and Engineering Data. 2013;58:2248–2253.
29. Cao JS, Lin JX, Fang F, Zhang MT, Hu Z. A new absorbent by modifying walnut shell for the removal of anionic dye: Kinetic and thermodynamic studies. Bioresoure Technology. 2014;163:199–205.

30. Wang BH, Sun H, Zhu J, Wang LL, Chen S. Bis (2-mercapto-ethyl) amine modification of macroporous sulfonic resin catalyst in bisphenol-a synthesis. AIChE Journal. 2013;59:3816–3823.
31. Kumar PS, Ramalingam S, Abhinaya RV, Kirupha SD, Murugesan A, Sivanesan S. Adsorption of metal ions onto the chemically modified agricultural waste. Clean-Soil Air Water. 2012;40:188–197.
32. Kumar PS, Senthamarai C, Durgadevi A. Adsorption kinetics, mechanism, isotherm, and thermodynamic analysis of copper ions onto the surface modified agricultural waste. Environmental Progress and Sustainable Energy. 2014;33:28–37.

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