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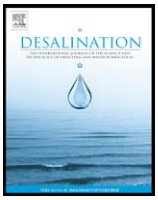

Removal of Pb (II) from aqueous solutions by adsorption onto modified areca waste: Kinetic and thermodynamic studies

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ABSTRACT

The removal of Pb^{2+} in modified areca waste from aqueous solutions with the Fenton reagent was investigated. Experiments were carried out as function of contact time and initial concentration (4–12 mg/L). The equilibrium adsorption data of Pb^{2+} on MAW were analyzed by Langmuir and Freundlich models. The equilibrium adsorption data were well described by the Freundlich and Langmuir isotherms. The monolayer adsorption capacity was found to be 3.37 mg/g at pH 6.6 and 323 K. Adsorption data were modeled using the pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetics equations. The experimental data were fitted well the pseudo-second-order kinetics. Isotherms had also been used to obtain the thermodynamic parameters such as free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) of adsorption. The negative value of ΔG^0 indicates the feasibility and spontaneity of the adsorption process. The positive ΔH^0 suggests the endothermal nature of the adsorption. The positive values of ΔS^0 reflects the affinity of MAW towards Pb^{2+}. Desorption studies revealed that the MAW can be regenerated using HNO_3 by adjusting pH.

1. Introduction

Heavy metal toxicity has become a major concern today due to its deleterious effects on health and environment. Lead is one of the major environmental pollutants because of its presence in automobile fuel and subsequent emission into the atmosphere in the exhaust gases. Lead is accumulated in human system through many ways such as breathing air from industrial environment, ingesting plants or food grown on contaminated soils and breathing in fumes from hobbies that use lead (leaded-glass and ceramics) [1]. Drinking those that contain Pb^{2+} ions for a long term, even if in a very low concentration, could lead to a wide range of spectrum health problems, such as renal failure, coma, nausea, cancer, convulsions and subtle effects on metabolism and intelligence [2,3].

Physical and chemical processes have been extensively studied to remove the heavy metal pollutants from wastewaters at high concentrations. Some of these processes are adsorption, coagulation, flotation, biosorption, chemical precipitation, solvent extraction, reverse osmosis, ion exchange, chemical oxidation and reduction, ultra filtration and electrochemical methods. Among the various water-treatment techniques described, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness.

Considerable attention has been devoted to the study of removal of heavy metal ions from solution by adsorption using low cost, non-conventional alternative materials which used to be considered as waste such as grape stalk, nut wastes, tree barks, coconut shell, sawdust, chestnut pellicle, areca waste, peanut skins, peat, sugarcane, lignin and others [4–20].

Areca nut is known since the pre-Christian era and is still a very popular chewing nut in different areas of the world. *Areca cathecu* produces the well-known betel nut of commerce, which is in great demand in Eastern countries for chewing. In China, areca is mainly produced in the provinces Hainan, Fujian, Yunnan, Guangxi, Taiwan, etc. In 2003, the total output of dried fruit 55 000 t, more than 1 billion yuan output value of betel nut of tropical cash crops in Hainan Province. Hunan Province betel nut processing industry employed 20 million people, the annual output value of more than 1 billion yuan. They can live outside southern Florida and other subtropical and tropical regions. *Areca catechu* produces the well-known betel nut of commerce, which is in great demand in eastern countries for chewing [10]. The ripe fruit is reaped from the end of spring to the beginning of autumn. Boil the fruit in water, dry, peel and remove the seeds, dry them in the sun, soak thoroughly and slice or pound for use. The AW was collected from the betel nut after chewing.

In continuation of our studies, this article researched on the kinetic and thermodynamic study of the adsorption of Pb^{2+} on MAW. A

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kinetic analysis was carried out using the Lagergren pseudo-first-order and Ho's pseudo-second-order kinetic models. Standard thermodynamic models were used to obtain thermodynamic parameters.

2. Materials and methods

2.1. Modified areca waste

The adsorbent was made of Fenton modified areca waste at variable particle sizes. Argun and Dursun [22] studied the proportions of lignin increased and cellulosic materials, hemicellulosic materials, and extractives decreased during the modification process. This change is beneficial because previous research [23] has demonstrated that heavy metals are adsorbed by lignin rather than by cellulose and hemicellulose. In accordance with the reference [21,22] Fenton reagent (Fe^{2+}/H_2O_2 ratio = 0.01) used to increase the proportion of active surface. Washed and dried AW (20 g) was poured into a 500 mL beaker containing 250 mL Fenton's reagents solutions and stirred at 200 rpm for all modification experiments. After that, the solution was filtered and AW was taken and washed for several times with distilled water. Then the treated AW was dried at 60 °C for 8 h and then allowed to cool in the desiccator for use.

2.2. Apparatus and instrumentation

The lead concentrations in the sample were determined using atomic adsorption spectrophotometer (Perkin-Elmer 700). The pH measurements were made using a pH meter (Multiline 330i). All experimental treatments in this study were conducted in acid-washed (2% HNO_3) polycarbonate labware.

2.3. Preparation of metal solutions

The synthetic solutions were all prepared by diluting Pb^{2+} standard stock solutions (concentration 1000 ± 2 mg/L) obtained by dissolving $Pb(NO_3)_2$ in deionized water. Fresh dilutions were used in each experiment.

2.4. Adsorption experiments

Adsorption experiments were carried out by adding a fixed amount of adsorbent (1.000 g) to a series of 250 mL beakers filled with 100 mL initial Pb^{2+} concentrations ranging from 4 to 12 mg/L (4 mg/L interval). These samples were then mounted on a shaker and shaken (200 rpm) with a required adsorbent time at ambient temperature and required pH. At predetermined time intervals, samples were collected utilizing a 0.45-μm Nucleopore polycarbonate membrane filters. The final metal concentration in the filtrates as well as in the initial solution was determined by AAS. The sorbed metal concentrations were obtained from the difference of the initial and final metal concentrations in solution. No efforts were made to maintain the solution pH while metal ions were being sorbed.

The percentage adsorption of lead was calculated according to

$$\textit{Removal lead}\ (\%) = \frac{(C_0 - C_e)}{C_0} \times 100\% \tag{1}$$

And the amount of Pb^{2+} adsorbed on the adsorbent was calculated using the following expression:

The lead adsorption capacity of the MAW was calculated as Eq. (2) below:

$$q = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where q, adsorption capacity per unit mass of MAW (mg/g); C_0, initial concentration of lead in the aqueous solution (mg/L); C_e is the final equilibrium concentration of test solution (mg/L); m, mass of MAW (g); and V, volume of sample (L).

In order to investigate the desorption capacity of Pb^{2+} from MAW. The exhausted MAW was dried at 60 °C and dispersed into 100 mL deionized water. The pH value of the solution was adjusted to 1.5 using HNO_3 solution. After the solutions reached equilibrium, the Pb^{2+} concentrations were measured and the desorption results were then obtained.

Each experiment was carried out in triplicate and the average results are presented in this study.

2.5. Adsorption isotherms

2.5.1. Langmuir isotherm

Langmuir's isotherm model is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The Langmuir treatment is based on the assumption that a maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface, which is represented as follows:

$$\frac{1}{q_e} = \frac{1}{ab} \cdot \frac{1}{C_e} + \frac{1}{b} \tag{3}$$

where q_e, the amount of metal per unit of MAW at equilibrium (mg/g); a, a constant related to the affinity of the binding sites (L/mg); b, the maximum amount of metal ion per unit of MAW (mg/g); C_e, the residual metal concentration in solution at equilibrium (mg/L). These constants are evaluated from the slope and intercept of the linear plots of $1/q_e$ versus $1/C_e$, respectively.

Based on the further analysis of Langmuir equation, the dimensionless parameter of the equilibrium or adsorption intensity (R_L) can be expressed by

$$R_L = \frac{1}{1 + aC_0} \tag{4}$$

where C_0, the initial amount of adsorbate (mg/L). The R_L parameter is considered as a more reliable indicator of the adsorption. There are four probabilities for the R_L value: (i) for favorable adsorption, $0 < R_L < 1$, (ii) for unfavorable adsorption, $R_L > 1$, (iii) for linear adsorption, $R_L = 1$, and (iv) for irreversible adsorption, $R_L = 0$ [24].

2.5.2. Freundlich isotherm

The Freundlich equation has been widely used for isothermal adsorption. This is a special case for heterogeneous surface energies in which the energy term, a, in the Langmuir equation varies as a function of surface coverage, q_e, strictly due to variations in heat of adsorption. The Freundlich isotherm is represented by Eq. (5).

$$\lg q_e = \lg K^0 + \frac{1}{n} \lg C_e \tag{5}$$

where q_e, the amount of adsorbed per unit weight (mg/g); K^0, Freundlich constant related to adsorption capacity; C_e, the equilibrium concentration (mg/L); n, Freundlich constant related to adsorption intensity.

2.6. Adsorption kinetics

To analyze the adsorption rate of lead onto MAW, a pseudo-first-order rate equation was used to simulate the kinetic adsorption [25,26]:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \tag{6}$$

where K_1 (min^{-1}) is the rate constant of the pseudo-first-order sorption, q_e (mg/g) is the amount of heavy metals adsorbed on the

MAW surface at equilibrium, and q (mg/g) is the amount of heavy metals adsorbed at any time t (min).

The pseudo-second-order reaction rate equation has the form [27,28]:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \tag{7}$$

where q_t is the amount of metal ions adsorbed (mg/g) at any given time t (min), q_e is the amount of metal ion adsorbed (mg/g) at equilibrium and K_2 is the second-order reaction rate constant for adsorption (g/(mg·min)). The following expression denotes the initial sorption rate v_0 (mg/(g min)) [27]:

$$v_0 = K_2 q_e^2 \tag{8}$$

The intraparticle diffusion model [29,30] was considered in order to determine the participation of this process in the sorption of lead by MAW. According to this model, the plot of uptake (q_t), versus the square root of time ($t^{0.5}$) should be linear if intraparticle diffusion is involved in the overall adsorption mechanism. Furthermore, if this line passes through the origin then the intraparticle diffusion is the rate controlling step of the process. The initial rate of intraparticle diffusion, K_d, can be calculated in the following way:

$$q_t = Kt^{0.5} + C \tag{9}$$

where q_t is the amount of sorbate on the surface of the sorbent at time t (mg/g), K_d is the intraparticle rate constant (mg/(g min$^{0.5}$)) and t is the time (min). If intraparticle diffusion is rate-limited, then plots of adsorbate uptake q_t versus the square root of time ($t^{0.5}$) would result in a linear. The coefficients K and C values can be obtained from these plots.

3. Results and discussion

3.1. Effects of initial concentration and time

Fig. 1 shows the effect of contact time on lead adsorption onto MAW. One can see that the adsorption is rapid in the initial 30 min of the contact time. Sixty minutes is almost enough to attain equilibrium for the three concentrations of lead used in this study. The initial steep adsorption curve suggests that the adsorption occurs rapidly on the surface of MAW. The adsorption becomes slow subsequently because of the longer diffusion into the inner cavities in exiguous solutions. Such slow diffusion will lead to a slow increase in the adsorption curve at later stages. At low concentrations, sufficient adsorption sites are available for adsorption of the Pb(II) metal ions. Therefore, the fractional adsorption was observed to be independent of initial metal ion concentration. However, at higher concentrations the numbers of heavy metal ions are relatively higher compared to availability of adsorption sites. Hence the percentage removal of Pb(II) depends on the initial metal ion concentration and decreases with an increase in initial metal ion concentration. According to the above results, the shaking time was fixed for 120 min for the rest of the batch experiments to make sure that equilibrium was reached.

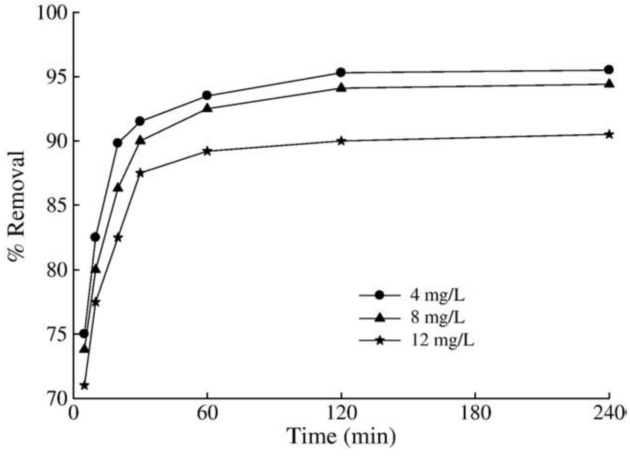

Fig. 1. Effects of initial concentration and time on lead adsorption onto MAW (MAW dose = 10 g/L; pH = 6.6; T = 293 ± 2 K).

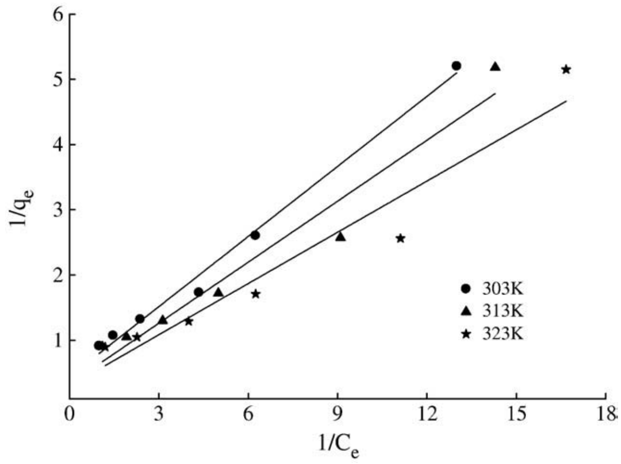

Fig. 2. Fitting lines of the Langmuir adsorption isotherms of Pb^{2+} onto MAW at various temperatures (MAW dose = 10 g/L; pH = 6.6).

3.2. Adsorption isotherms

The equilibrium data obtained for the adsorption of Pb^{2+} onto MAW were fitted to linear Langmuir equation. Linear plot of $1/q_e$ versus $1/C_e$ (Fig. 2) was examined to determine b and a values. The experimental data were fitted to the Langmuir equation (Table 1), and the parameter ($0<R_L<1$) indicates that the MAW is a suitable adsorbent for the adsorption of Pb^{2+} from aqueous solution.

The equilibrium data were fitted to linear Freundlich equation for the adsorption of Pb^{2+} onto MAW (Fig. 3). A fairly satisfactory empirical isotherm can be used for nonideal adsorption because the coefficient of determination (R^2) was 0.9002–0.9546 (Table 1). From the linear plot of Freundlich isotherm, K^0 and $1/n$ were found as 1.244–1.546 and 0.6267–0.6621, respectively. The values of $0.1<1/n<1$ show favorable adsorption of cadmium ions onto MAW. The correlation coefficients show that the Langmuir model is better fitted than the Frendlich.

3.3. Adsorption kinetics

The validity of the order of adsorption process was based on the two criteria, first based on the regression coefficient and secondly

Table 1
Parameters of Langmuir and Freundlich models.

	Langmuir isotherm constants			Freundlich isotherm constants		
T(K)	a	b	R^2	K^0	$1/n$	R^2
303	1.22	2.28	0.9914	1.244	0.6621	0.9546
313	1.04	3.08	0.9535	1.423	0.6522	0.9234
323	1.13	3.37	0.9369	1.546	0.6267	0.9002

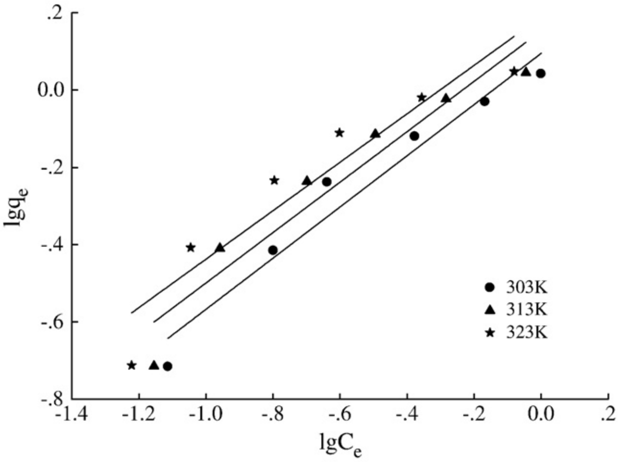

Fig. 3. Fitting lines of the Freundlich adsorption isotherms of Pb^{2+} onto MAW at various temperatures (MAW dose = 10 g/L; pH = 6.6).

based on the calculated q_e values. The calculated q_e ($q_{e(cal)}$) was obtained from the constant term of Eq. (6) and from the slope of Eq. (7) for the first- and second-order equations, respectively. The value of K_1 can be determined by the intercept of linear plots of versus. The linear plot of $\log(q_e-q)$ versus t (Fig. 4) was achieved and the K_1 values were calculated from the intercepts in Table 2. The correlation coefficients obtained were in the range of 0.8934–0.9817 and the $q_{e(cal)}$ values obtained from the first-order-kinetic model did not agree with the experimental ($q_{e(exp)}$) values as shown in Table 2. This indicates that the adsorption of Pb^{2+} onto MAW do not follow the first-order-kinetic model. The linear plots of t/q_t versus t in Fig. 5 yielded the second-order rate constant k_2. The $q_{e(cal)}$ values from the slope of the equation had an agreement with the $q_{e(exp)}$ values as seen in Table 2. Moreover, the correlation coefficients for the second-order-kinetic model were very high ($R^2 = 1.0000$). Thus, it is inferred that the adsorption system belongs to the second-order-kinetic model.

The intraparticle diffusion rate, obtained from the plots q_t versus $t^{0.5}$. The plots are shown in Fig. 6. As can be seen from Fig. 6 for the system investigated, the relationships are not linear. All plots have an initial curved portion, followed by intermediate linear portion and a plateau. The adsorption was controlled by three different stages [31]: the first sharper portion being a rapid external surface adsorption, the second linear portion being a gradual adsorption where intraparticle diffusion is the rate limiting factor, and the final portion being final equilibrium stage due to low concentration of lead in solution phase as well as less number of available adsorption sites.

Table 2
Parameters calculated using the pseudo-first-order and the pseudo-second-order models for the adsorption of Pb^{2+} on MAW.

Concentration	Pseudo-first-order model				Pseudo-second-order model			
	$q_{e(exp)}$	$q_{e(cal)}$	K_1	R^2	ν_0	$q_{e(cal)}$	K_2	R^2
4 mg/L	0.28	0.069	0.0387	0.9743	0.240	0.386	1.612	1.0000
8 mg/L	0.62	0.149	0.0368	0.9817	0.412	0.764	0.706	1.0000
12 mg/L	1.14	0.169	0.0309	0.8934	0.669	1.096	0.557	1.0000

3.4. Thermodynamic studies

The thermodynamic parameters, the values of enthalpy, ΔH^0, and entropy, ΔS^0, and Gibbs free energy, ΔG^0, of the sorption are useful in defining whether the sorption reaction is endothermic or exothermic, and spontaneity of the adsorption process. The parameters can be calculated from the binding, *ab*, obtained from the Langmuir's equation, using the following equations [32]:

$$\Delta G^0 = -RT \ln ab \tag{10}$$

The ΔH^0 values are calculated from the slopes of the linear variation of ln*ab* versus $1/T$ (in Fig. 7):

$$\ln ab = -\frac{\Delta H^0}{RT} + \text{constant} \tag{11}$$

The values of ΔS^0 were calculated from:

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \tag{12}$$

where R (8.3145 J mol−^{1} K−^{1}) is the ideal gas constant, and T (K) is the temperature. Relevant data calculated from Eqs. (10)–(12) are tabulated in Table 3. The adsorption of Pb^{2+} increases with the increase of temperature and the value of ΔH^0 is positive. The positive ΔH^0 value confirms that the absorption process is endothermic for Pb^{2+}, which is an indication of the existence of a strong interaction between MAW and Pb^{2+}. The ΔG^0 for the adsorption process was

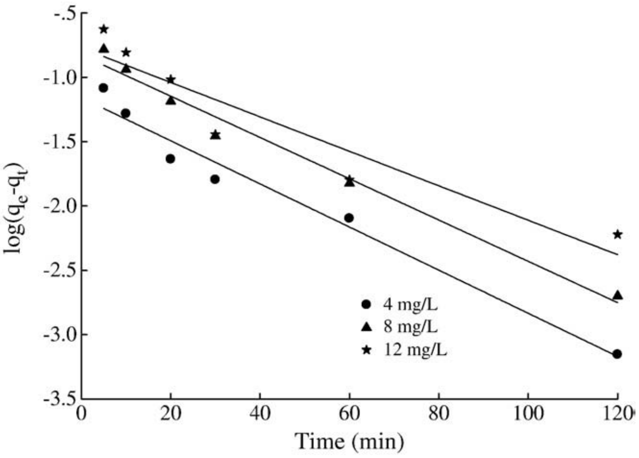

Fig. 4. Pseudo-first-order kinetics for adsorption of lead onto MAW (MAW dose = 10 g/L; pH = 6.6; $T = 293 \pm 2$ K).

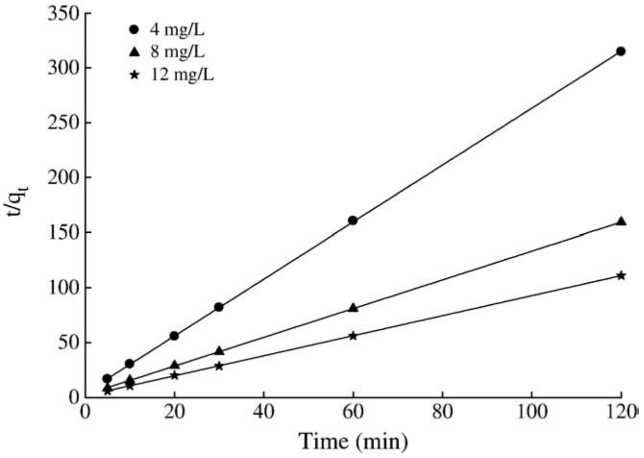

Fig. 5. Pseudo-second-order kinetics for adsorption of Pb^{2+} onto MAW (MAW dose = 10 g/L; pH = 6.6; $T = 293 \pm 2$ K).

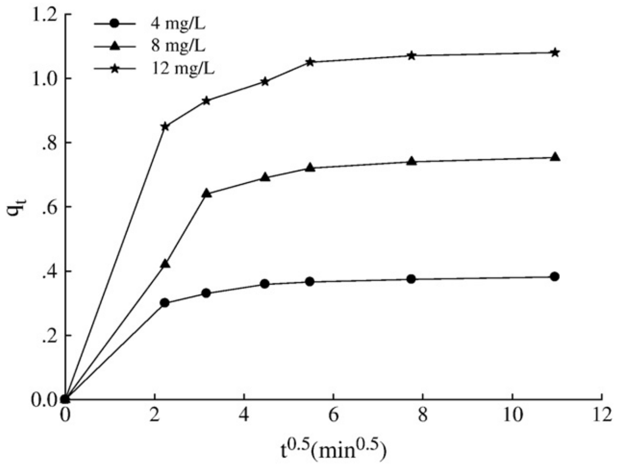

Fig. 6. Intraparticle diffusion kinetics for adsorption of lead onto MAW (MAW dose = 10 g/L; pH = 6.6; $T = 293 \pm 2$ K).

obtained as −2.58, −3.03 and −3.59 kJ/mol at 303, 313 and 323 K, respectively. The negative ΔG^0 values at different temperatures were due to the fact that the adsorption process is spontaneous. The value of ΔG^0 decreased with an increase in temperature, indicated that the spontaneous nature of the adsorption of Pb^{2+} is inversely proportional to the temperature. Generally, the absolute magnitude of the change in free energy for adsorption is between 0 and −20 kJ/mol. Adsorption type can be explained as physisorption [33,34]. The positive values of ΔS^0 reflect the affinity of adsorbent material towards Pb^{2+}.

3.5. Desorption of Pb^{2+} from MAW

A desorption study is also important because it is useful in the recycling of the adsorbent and recovery of heavy metals. The results (Table 4) show that the percentage adsorption of Pb^{2+} onto MAW decreases with the increase of initial Pb^{2+} concentration in the solution, with a decrease slightly in Pb^{2+} loading and keeps high. These results indicate that Pb^{2+} adsorption is reversible and can be desorbed easily by adjusting the pH. Thus the MAW can be employed repeatedly in the heavy metal adsorption.

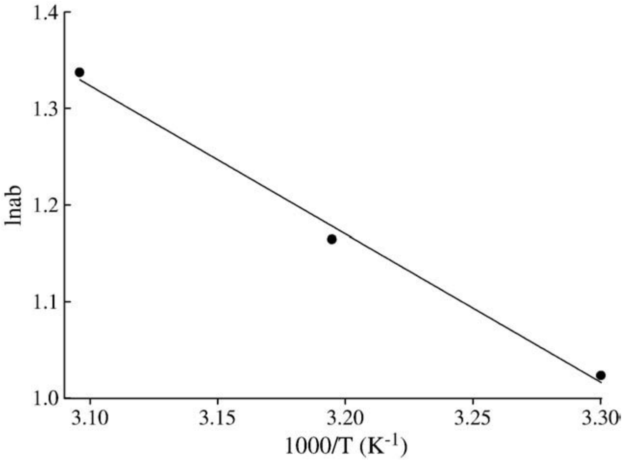

Fig. 7. Plot of lnab vs. 1/T for Pb^{2+} adsorption onto MAW ($C_0 = 8$ mg/L; MAW dose = 10 g/L; pH = 6.6; $T = 293 \pm 2$ K).

Table 3
Thermodynamic parameters for lead adsorption onto MAW.

ΔH^0(KJ mol^{-1})	12.9
ΔS^0(KJ mol^{-1} K^{-1})	0.034
$-\Delta G^0$	
303 K	2.58
313 K	3.03
323 K	3.59

Table 4
Desorption of Pb^{2+} from loaded MAW.

C_0 (Pb^{2+}) (mg/L)	% Adsorption	After desorption (mg/L)	% Desorption
4	95.5	3.76	98.4
8	94.4	7.33	97.1
12	90.5	10.32	95

4. Conclusions

In the light of the finding of this work, the following main conclusions can be stressed:

(1) The Pb^{2+} uptake at equilibrium by MAW could be described by both the Langmuir and the Freundlich adsorption isotherms. The correlation coefficients show that the Langmuir model is better fitted than the Frendlich.
(2) The adsorption process follows a pseudo-second-order kinetics.
(3) The negative value of ΔG^0 indicates the feasibility and spontaneity of the adsorption process. The positive ΔH^0 suggests the endothermal nature of the adsorption. The positive values of ΔS^0 reflects the affinity of MAW towards Pb^{2+}.
(4) Pb^{2+} adsorption is reversible and can be desorbed from MAW by adjusting the pH values of the solution.

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References

[1] E.I. Unuabonah, K.O. Adebowale, B.I. Olu-Owolabi, Kinetic and thermodynamic studies of the adsorption of lead (II) ions onto phosphate-modified kaolinite clay, J. Hazard. Mater. 144 (2007) 386–395.
[2] M.N. Rashed, Lead removal from contaminated water using mineral adsorbents, Environmentalist 21 (2001) 187–195.
[3] Y.H. Li, Z. Di, J. Ding, D. Wu, Z. Luan, Y. Zhu, Adsorption thermodynamic, kinetic and desorption studies of Pb^{2+} on carbon nanotubes, Water Res. 39 (2005) 605–609.
[4] I. Villaescesa, N. Fiol, M. Martínez, N. Miralles, J. Poch, J. Serarols, Removal of copper and nickel ions from aqueous solutions by grape stalk wastes, Water Res. 38 (2004) 992–1002.
[5] D. Parajuli, C.R. Adhikari, H. Kawakita, S. Yamada, K. Ohto, K. Inoue, Chestnut pellicle for the recovery of gold, Bioresour. Technol. 100 (2009) 1000–1002.
[6] B.G.P. Kumar, K. Shivakamy, L.R. Miranda, M. Velan, Preparation of steam activated carbon from rubberwood sawdust *(Hevea brasiliensis)* and its adsorption kinetics, J. Hazard. Mater. B 136 (2006) 922–929.
[7] G. Palma, J. Freer, J. Baeza, Removal of metal ions by modified *Pinus radiate* bark and tannins from water solutions, Water Res. 37 (2003) 4974–4980.
[8] F. Qin, B. Wen, X.Q. Shan, Y.F. Xie, T. Liu, S.Z. Zhang, S.U. Khan, Mechanisms of competitive adsorption of Pb, Cu and Cd on peat, Environ. Pollut. 144 (2006) 669–680.
[9] D. Mohan, K.P. Singh, Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—an agricultural waste, Water Res. 36 (2002) 2304–2318.

[10] W. Zheng, X.M. Li, F. Wang, Q. Yang, P. Deng, G.M. Zeng, Adsorption removal of cadmium and copper from aqueous solution by areca—a food waste, J. Hazard. Mater. 157 (2008) 490–495.

[11] M.A. Farajzadeh, A.B.y Monji, Adsorption characteristics of wheat bran towards heavy metal cations, Sep. Purif. Technol. 38 (2004) 197–207.

[12] Y. Wu, S.Z. Zhang, X.Y. Guo, H.L. Huang, Adsorption of chromium(III) on lignin, Bioresour. Technol. 99 (2008) 7709–7715.

[13] A.T.M. Din, B.H. Hameed, A.L. Ahmad, Batch adsorption of phenol onto physiochemical-activated coconut shell, J. Hazard. Mater. 161 (2009) 1522–1529.

[14] D. Kalderis, D. Koutoulakis, P. Paraskeva, E. Diamadopoulos, E. Otal, J.O.d. Valle, C. Fernández-Pereira, Adsorption of polluting substances on activated carbons prepared from rice husk and sugarcane bagasse, Chem. Eng. J. 144 (2008) 42–50.

[15] D. Sud, G. Mahajan, M.P. Kaur, Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions—a review, Bioresour. Technol. 99 (2008) 6017–6027.

[16] E.I. El-Shafey, Removal of Se(IV) from aqueous solution using sulphuric acid-treated peanut shell, J. Environ. Manage. 84 (2007) 620–627.

[17] M. Soleimani, T. Kaghazchi, Adsorption of gold ions from industrial wastewater using activated carbon derived from hard shell of apricot stones—an agricultural waste, Bioresour. Technol. 99 (2008) 5374–5383.

[18] S. Ricordel, S. Taha, I. Cisse, G. Dorange, Heavy metals removal by adsorption onto peanut husks carbon: characterization, kinetic study and modeling, Sep. Purif. Technol. 24 (2001) 389–401.

[19] W. Zheng, X.M. Li, Q. Yang, G.M. Zeng, X.X. Shen, Y. Zhang, J.J. Liu, Adsorption of Cd (II) and Cu(II) from aqueous solution by carbonate hydroxylapatite derived from eggshell waste, J. Hazard. Mater. 147 (2007) 534–539.

[20] D.X. Liao, W. Zheng, X.M. Li, Q. Yang, X. Yue, L. Guo, G.M. Zeng, Removal of lead(II) from aqueous solutions using carbonate hydroxyapatite extracted from eggshell waste, J. Hazard. Mater. 177 (2010) 126–130.

[21] P. Brown, I.A. Jefcoat, D. Parrish, S. Gill, E. Graham, Evaluation of the adsorptive capacity of peanut hull pellets for heavy metals in solution, Adv. Environ. Res. 4 (2000) 19–29.

[22] M.E. Argun, S. Dursun, A new approach to modification of natural adsorbent for heavy metal adsorption, Bioresour. Technol. 99 (2008) 2516–2527.

[23] I. Gaballah, G. Kilbertus, Recovery of heavy metal ions through decontamination of synthetic solutions and industrial effluents using modified barks, J. Geochem. Explor. 62 (1998) 241–286.

[24] Y.S. Ho, C.T. Huang, H.W. Huang, Equilibrium sorption isotherm for metal ions on tree fern, Process Biochem. 37 (2002) 1421–1430.

[25] S. Lagergren, Zur, Theorie der sogenannten adsorption geloster stoffe, K. Sven. Vetenskapsakad. Handl. 24 (1898) 1–39.

[26] Y.S. Ho, Citation review of Lagergren kinetic rate equation on adsorption reactions, Scientometrics 59 (2004) 171–177.

[27] G. McKay, Y.S. Ho, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[28] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115–124.

[29] W.J. Weber, J.C. Morriss, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. Am. Soc. Civil Eng. 89 (1963) 31–60.

[30] Q. Sun, L. Yang, The adsorption of basic dyes from aqueous solution on modified peat–resin particle, Water Res. 37 (2003) 1535–1544.

[31] W.S.W. Ngah, M.A.K.M. Hanafiah, Adsorption of copper on rubber (*Hevea brasiliensis*) leaf powder: kinetic, equilibrium and thermodynamic studies, Biochem. Eng. J. 39 (2008) 521–530.

[32] C. Namasivayam, R.T. Yamuna, Adsorption of chromium by a low-cost adsorbent: biogas residual slurry, Chemosphere 30 (1995) 561–578.

[33] H. Nollet, M. Roels, P. Lutgen, P.V.D. Meeren, W. Verstraete, Removal of PCBs from wastewater using fly ash, Chemosphere 53 (2003) 655–665.

[34] V. Padmavathy, Biosorption of nickel(II) ions by baker's yeast: kinetic, thermodynamic and desorption studies, Bioresour. Technol. 99 (2008) 3100–3109.