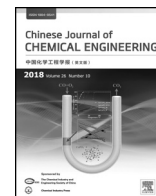




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Article

Pressure relief-dipping-microwave assisted polymerization of melamine-L-aspartic acid resin at activated carbon for purification of L-threonine fermented crude product☆

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ABSTRACT

L-threonine (L-Thr) obtained by fermentation often contains vestigial hydrosoluble Pb(II), Fe(II), L-glutamic acid (L-Glu) etc., which affect the product quality. Poly melamine and L-aspartic acid (L-Asp) resin functional coconut shell activated carbon composite (PMA/AC) was prepared by a pressure relief-dipping-microwave assisted polymerization method for the simultaneous removals. The adsorption capacities of Pb(II), Fe(II) and L-Glu could reach to 82.34 mg·g⁻¹, 57.82 mg·g⁻¹ and 102.58 mg·g⁻¹ at conditions of pH 5.0, 45 °C and 4 h with an initial concentration of 0.01 mol·L⁻¹, respectively. The present PMA/AC was successfully used to the simultaneous removals of vestigial Pb(II), Fe(II) and L-Glu from the fermented crude product solution of L-Thr. Moreover, the PMA/AC was carefully characterized by FE-SEM, IR *et al.* analysis techniques, the results show that abundant PMA particles evenly distributed at the inner and outside surface of AC with a size of (50 ± 20) nm.

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1. Introduction

L-Threonine (L-Thr) is an essential amino acid that is widely used in animal feeds, human foods, cosmetics as well as pharmaceutical industries, which has exhibited steadily increasing global demand in recent years [1,2]. In the conventional industrial production, L-Thr could be obtained from fermentation method as following steps [3–7]: The zymotic fluid of L-Thr respectively undergoes membrane separation to remove bacteria, solid insolubles and macromolecular substances [5–7]; adsorption by naked active carbon to decolor [6,7]; followed evaporation, crystallization at isoelectric point and drying steps to obtain product. Because the hydrosoluble Pb(II), Fe(II), As (V) and L-Glu in the zymotic fluid of L-Thr could not be fully separated by membrane or naked active carbon, which could be co-deposited in the crystallization processes, the crude product of L-Thr still contains the vestigial impurities [8]. Thus, people often have to dissolve the crude product of L-Thr, and repeat the processes to obtain medical grade L-Thr with higher expenditure. Although some promising electrodialysis membrane separation techniques were reported for the desalting of amino acids fermentative

solution, the researches are mainly in the laboratory stage [9–12]. In the present industrial production level, it is essential to prepare functional activated carbon composite for the simultaneous removals from the fermentation crude product of L-Thr in terms of improving product quality with lower cost materials.

Gelatinous poly L-aspartic acid (L-Asp) is an excellent heavy metal ions chelator, which was widely used for the removal of heavy metals from aqueous solution due to its nontoxic, biodegradable and hydrophilic properties [13], but it could not be recovered after use. Moreover, L-Glu and L-Asp belong to acidic amino acid with similar properties [14]. On the other hand, powdery poly melamine resin is a medium-strong heavy metal ion chelator with weak hydrophilicity [15], it is difficultly separated from aqueous solution too.

Based on the above facts, coconut shell carbon probably is a useful support with porous structure and good biocompatibility [16], which was used for decoloration of food industry [6,7]. The poly melamine and L-Asp resin (PMA) displays solid state. PMA functional coconut shell activated carbon composite probably is a promising multifunction adsorbent with seemly hydrophilicity, biocompatibility and separability (PMA/AC), which could be used for the simultaneous removals of vestigial Pb(II), Fe(II) and L-Glu from the crude product solution of L-Thr except decoloration. There has no any report up to now. In this work, PMA/AC was prepared by a pressure relief-dipping- microwave assisted method. The behaviors of Pb(II), Fe(II), L-Glu and L-Thr were respectively investigated using PMA/AC in detail, and the simultaneous removals were performed from the crude product solution of L-Thr.

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2. Experiment

2.1. Chemicals and apparatus

Coconut shell activated carbon (AC) was obtained from Hengxin Environmental Protection Material Company of HuaiBei City. Melamine (ML), L-aspartic acid (L-Thr), L-glutamic acid (L-Glu), L-aspartic acid (L-Asp), polyvinyl alcohol (PVA), sodium dodecyl sulfate (SDS), $\text{Pb}(\text{NO}_3)_2$, FeCl_2 , ethylene diamine tetraacetic acid (EDTA), formaldehyde and all other chemicals were produced by Chemical Reagent Company of Shanghai products (China, Shanghai). All chemicals were of analytical grade. Real L-threonine sample was obtained from Shantou City Jiahe Biologic Technology Co. Ltd. Doubly distilled water was used as solvent to prepare all solutions.

The step of synthesis was conducted with a WBFY-201 Microwave Reactor (Shanghai Yuezhong Instrument Equipment Co. Ltd., China). Field emission scanning electron microscope (FE-SEM) images were performed at a JSM-600 field emission scanning electron microanalyser (JEOL, Japan). Infrared spectra (IR) were obtained at IR 200 (Nicolet America). Thermogravimetric Analysis (TG) was collected using BOEN-021200. Plasma mass spectrometer (ICP) was obtained by Agilent 7500 ICP-MS (Agilent, America). X-ray photoelectron spectroscopy (XPS) experiments were performed at an ESCALAB250Xi spectrometer (Thermo, America) with Mg-Alpha X-ray radiation as the source for excitation. The concentrations of amino acids could be determined using S-4330D amino acid analyzer (Sykam, Germany).

2.2. Preparation of PMA/AC

The preparation of PMA/AC was performed as following steps. (1) 5 g AC was ultrasonically agitated for 7 h in 60 ml mixed acid solution of nitric acid and perchlorate acid (7:3) to form carboxyl-AC, which was washed by distilled water to neutral pH, and dried in vacuum at 100 °C for 4 h. 2.0 g carboxyl-AC was quickly put in 50 ml 1.0 mmol·L⁻¹ ethylenediamine to form amine-AC, which was washed by acetone and distilled water, and dried in vacuum at 0 °C in 6 h. (2) 1.0 g amine-AC was quickly immersed in 50 ml mixing solution including 0.25 g ML, 30 ml 37% formaldehyde, 0.08 g L-Asp, 0.20 g PVC, and 0.15 g SDS for 4 h. After the mixture was treated with microwave irradiation of 500 W for 1 h at pH 1.5, 0.14 g triethanolamine was added to finish the polymerization with continuous irradiation of 15 min at same condition. The mixture was kept at 4 °C for 12 h to demulsify, followed by filtration, cleaning and desiccation. As a result, melamine L-aspartic acid resin functional activated carbon composite could be obtained (singled as PMA/AC). As a comparison, PMA/AC was prepared by only microwave irradiation method too.

2.3. Specific surface area and pore properties of PMA/AC

The specific surface area and pore structure of PMA/AC were determined by N₂ adsorption–desorption isotherms at 77 K (Micrometrics ASAP 2020 system) after being vacuum dried at 100 °C with 12 h. The specific surface area was calculated by BET (Brunauer–Emmett–Teller) method. The pore size distribution (PSD) plots were recorded from the adsorption branch of the isotherm based on the Barrett–Joyner–Halenda (BJH) model. All data were summarized in Table S1. In the present material, the specific surface area and pore size of PMA/AC are decreased compared to those of naked active carbon.

2.4. Batch adsorption experiments

Batch experiments were respectively carried out in 100 ml beaker containing 30 ml solution and 0.06 g PMA/AC with different concentrations from 0.001 to 0.01 mol·L⁻¹ at desired pH. 0.1 mol·L⁻¹ HCl and 0.1 mol·L⁻¹ NaOH were used to adjust pH. The beaker was immersed in a thermostat water bath at a desired temperature. The adsorption of each sample was determined in triplicate, and the average was used to

evaluate the adsorbent capability. The adsorption capacity (q , mg·g⁻¹) was calculated by Eq. (1) [16,17]. The adsorption capacity at equilibrium (q_e) was calculated by Eq. (1). Where, C_0 : initial concentrations (mg·L⁻¹), C_e : equilibrium concentrations (mg·L⁻¹), q_e : adsorbate amount adsorbed per unit dry mass of adsorbent (mg·g⁻¹), V : the solution volume (L), and m : the adsorbent dry-weight (g).

$$q_e = \frac{(C_0 - C_e)V}{m_{\text{ads}}} \quad (1)$$

2.4.1. Adsorption kinetics

Lagergren pseudo-first-order model in Eq. (2) and pseudo-second-order model in Eq. (3) were used to investigate the kinetic models [15,18]. Where, q_{e1} (q_{e2}): amount adsorbed at equilibrium of the pseudo-first-order (pseudo-second-order), q_t : amount adsorbed at time t .

$$\lg(q_{e1} - q_t) = \lg q_{e1} - \frac{k_1 t}{2.303} \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}^2} + \frac{t}{q_{e2}} \quad (3)$$

2.4.2. Adsorption isotherms

Adsorption isotherms were described by the linear form of Langmuir Eq. (4) and Freundlich Eq. (5) [19]. Where, K_L : Langmuir isotherm parameter, K_F : Freundlich isotherm parameter, q_e : amount adsorbed at equilibrium, q_m : the maximum adsorption capacity of the adsorbent, n : heterogeneity parameter of the adsorbent surface.

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

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

2.5. Application

PMA/AC was put in the fermented crude product solution of L-Thr in order to simultaneously remove the vestigial Pb(II), Fe(II) and L-Glu at desired conditions.

2.6. Determination

In the batch adsorption experiments, the remaining concentrations of Pb(II) or Fe(II) in the solution were determined by titration against EDTA, and xylenol orange conducted as the indicator. Because the concentrations of Pb(II), Fe(II) and L-Glu are too low to be titrated in the fermented product solution of L-Thr, ICP was used to determinate Pb(II) and Fe(II). The concentrations of L-Glu and L-Thr could be determined using S-4330D amino acid analyzer (Sykam, Germany).

3. Result and Discussion

3.1. Characterizes

3.1.1. FE-SEM

Fig. 1 shows the FE-SEM images of AC (A) PMA/AC using only microwave irradiation (B) and pressure relief-dipping-microwave (C) polymerization methods. In Fig. 1A and inset, the surface of original AC is porous and smooth. In Fig. 1B and inset, although the outside surface of AC was almost coated by a great deal of PMA particles with a size of (70 ± 50) nm, only a few PMA particles could be observed at the inside surface of AC. However, in Fig. 1C, it could be readily seen that abundant PMA particles evenly distributed at the inner and outside surface of AC with a size of (70 ± 30) nm. It illustrated that the suggesting method was advantageous to form event PMA particles coated AC composite. The material in Fig. 1C was used in the following studies.

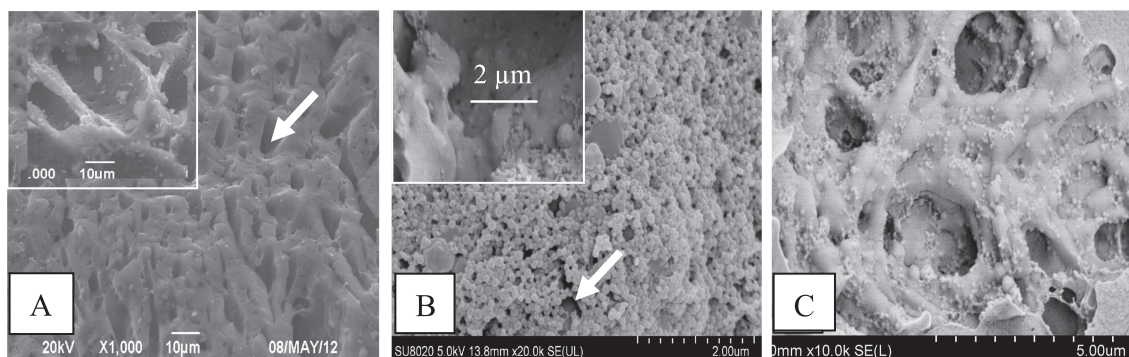


Fig. 1. FE-SEM of AC (A and inset) PMA/AC using only ultrasonic (B and inset) and pressure relief-dipping-ultrasonic (C) polymerization methods.

3.1.2. IR spectra

Fig. 2 shows the IR spectra of melamine (a), acid treated AC (b), aspartic acid (c) and PMA/AC (d). For melamine (a) [16,17], double peaks at 3475 cm^{-1} and 3423 cm^{-1} could be assigned to symmetrical and asymmetrical stretching vibrations of NH_2 group in melamine (a), two peaks at 1467 cm^{-1} and 819 cm^{-1} are caused by framework vibration and out-of-plane ring deformation for melamine molecule. A peak at 1638 cm^{-1} is matched to carbonyl ($\text{C}=\text{O}$) stretch of acid treated AC (b). For L-aspartic acid (c) [20], a peak at 2985 cm^{-1} is attributed to stretch vibration of $\text{N}-\text{H}$ in NH_3^+ pressed, and two peaks at 1603 cm^{-1} and 1517 cm^{-1} are related to flexural vibration of $-\text{NH}_2$, and double peaks at 1422 cm^{-1} and 1308 cm^{-1} are assigned to absorb peak of carboxyl anion ($-\text{COO}^-$). In curve d, the peaks at 3475 cm^{-1} (a), 2985 cm^{-1} and 1420 cm^{-1} (c) still could be observed, which could be traced back to melamine and aspartic acid. Furthermore, the peak at 1642 cm^{-1} ($\text{C}=\text{O}$) is obviously increased due to the amide reaction of melamine and aspartic acid with a little negative shift. Some peaks are overlapping from 1517 cm^{-1} to 1308 cm^{-1} . These illustrate the formation of PMA/AC compose, and the scheme could be suggested in Fig. 3.

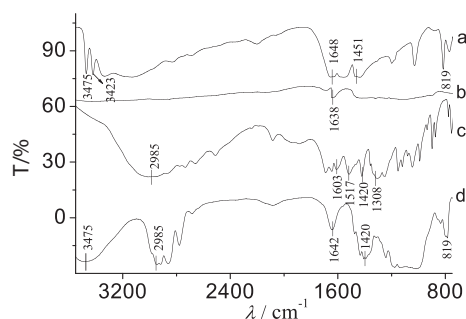


Fig. 2. IR spectra of melamine (a), acid treated AC (b), aspartic acid (c) and PMA/AC (d).

3.1.3. TG

Fig. 4 shows the TG curves of AC (a), PMA (c) and PMA/AC (b). There is a 12.6% mass loss before 400°C for AC (a) due to the loss of water or volatile. While 28.8% mass loss could be observed for only PMA before 360°C due to the decomposition of some polymer, the mass loss quickly reaches 89.1% from 360 to 460°C with an obvious jump, suggesting the collapse of PMA. In comparison with curves a and b, the mass loss jump of 37.1% could be seen for PMA/AC from 360 to 460°C with a positive shift of 30°C , curve a and curve c are similar after 460°C . These confirm that PMA was coated at the AC.

3.2. A batch adsorption experiment

3.2.1. pH effect

Fig. 5 shows the uptakes of Pb(II) (a), Fe(II) (b), L-Glu (c) and L-Thr (d) depending on pH at PMA/AC. The adsorption capacity of Pb(II) is raised to $89.2\text{ mg}\cdot\text{g}^{-1}$ at pH 5.3 (a). The adsorption capacity of Fe(II) could reached to $64.3\text{ mg}\cdot\text{g}^{-1}$ at pH 4.12 (b) ($\text{pH} > 6$, metal hydroxide precipitation could form). The uptakes probably attribute to the stable formation of resin-metal ion complex in slightly acidic media. The adsorption capacity of L-Glu is firstly decreased from pH 2 to pH 4 (c) due to their similar isoelectric point with electrostatic repulsion, then it increases to $125.9\text{ mg}\cdot\text{g}^{-1}$ at pH 7.0. It is noticeable that L-Thr could be adsorbed by PMA/AC too, the adsorption capacity of L-Thr reaches to $89.8\text{ mg}\cdot\text{g}^{-1}$ at pH 5.0, which is 74% of the largest capacity ($121.5\text{ mg}\cdot\text{g}^{-1}$). The present results show that their uptakes are pH dependent process. On the other hand, pH value of 7% fermented crude product solution of L-Thr is 5.0 (there is a little muddy while the concentration is more than 8%), thinking about the simultaneous removals, pH 5.0 could be selected.

3.2.2. Adsorption kinetics models

Fig. 6 shows the amount adsorbed of Pb(II) (a), Fe(II) (b), L-Glu (c) and L-Thr (d) depending on contact time. The uptakes are increased rapidly in the initial stage at initial concentration of $10.0\text{ mol}\cdot\text{L}^{-1}$, 25°C and pH 5.0. The 90% adsorption capacities of Pb(II) ($109.5\text{ mg}\cdot\text{g}^{-1}$), Fe(II) ($57.8\text{ mg}\cdot\text{g}^{-1}$), L-Glu ($102.6\text{ mg}\cdot\text{g}^{-1}$) and L-Thr ($89.3\text{ mg}\cdot\text{g}^{-1}$) could be obtained at contact times of 4 h, 4 h, 3 h and 3 h, respectively. Their adsorption equilibriums reach approximately within 12 h, respectively. In present study, the pseudo-first-order constant (k_1), pseudo-second-order constant (k_2), and linear correlation coefficient (R^2) were summarized in Table S2. The correlation coefficients (R^2) of Pb(II) and Fe(II) are considerable for the second-order model. This indicates that the second-order kinetic model nearly agreed with the experimental q_e value with chemisorption as the rate controlling step [15,19].

3.2.3. Adsorption isotherms

The adsorption isotherms could provide vital information in optimizing use of adsorbent. Fig. 7 shows the adsorption isotherms of Pb(II) , Fe(II) , L-Glu and L-Thr at different temperatures, and the corresponding parameters were summarized in Table S3. Langmuir isotherms well fitted to describe the four substance adsorption equilibria at PMA/AC. The maximum adsorption capacities (q_m) of Fe(II) , Pb(II) , L-Thr and L-Glu are 64.3 , 98.2 , 103.4 and $108.5\text{ mg}\cdot\text{g}^{-1}$ at 45°C . The maximum adsorbed capacities are increased with the increasing adsorption temperature, which meant that the increase in energy favors the adsorption at PMA/AC, and the sorption process is an endothermic character. The phenomenon was confirmed by the change of enthalpy as noted in thermodynamics of adsorption. The essential features of the Langmuir isotherm model

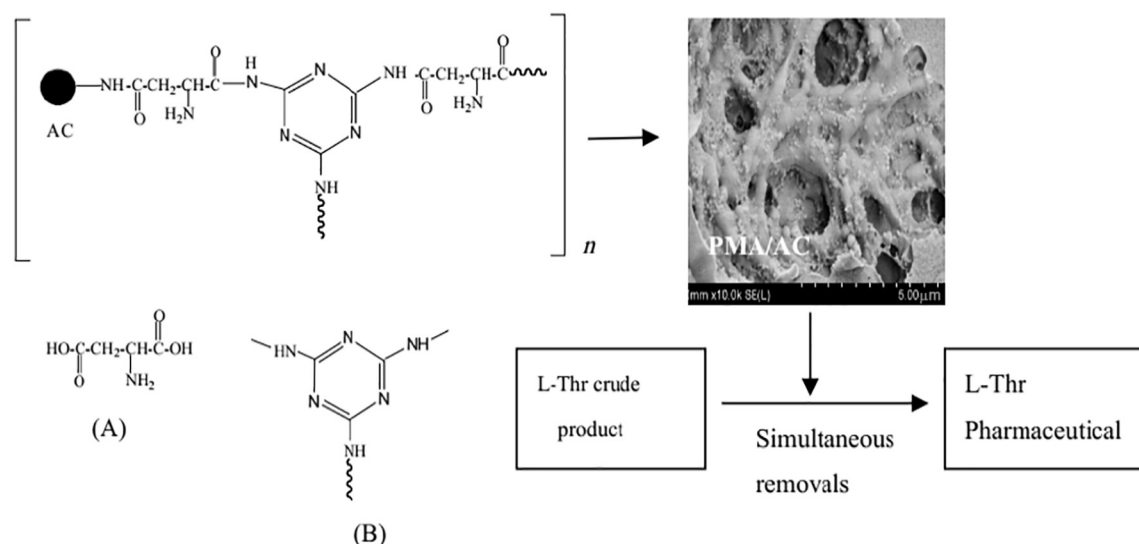


Fig. 3. Scheme of PMA/AC.

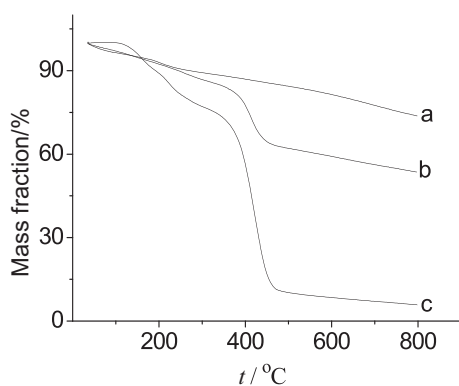
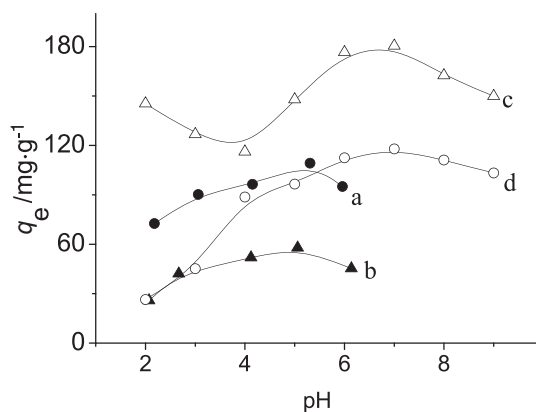
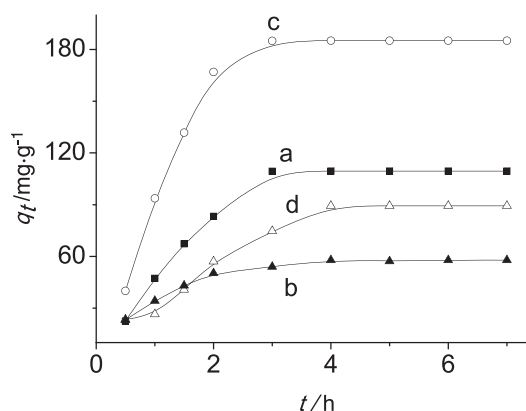


Fig. 4. Thermogravimetric analysis of AC (a), PMA/AC (b) and PMA (c).

Fig. 5. Uptakes of Pb(II) (a), Fe(II) (b), L-Glu (c) and L-Thr (d) depending on pH at PMA/AC with an initial concentration of $0.01 \text{ mol} \cdot \text{L}^{-1}$, 25°C and 4 h.

can be expressed with a dimensionless constant separation factor or equilibrium parameter R_L , which is defined by Eq. (6) [16,21]. Where, C_0 : initial concentration ($\text{mmol} \cdot \text{L}^{-1}$), K_L : Langmuir isotherm parameter ($\text{L} \cdot \text{mmol}^{-1}$) described above. R_L : isotherm slope. The R_L values could be classified as $R_L > 1$, $0 < R_L < 1$ and $R_L = 0$ suggests that adsorption is

Fig. 6. Adsorption capacities of L-Thr (a), Fe(II) (b), L-Glu (c) and Pb(II) (d) depending on contact time at initial concentration of $10.0 \text{ mmol} \cdot \text{L}^{-1}$, 25°C and pH 5.0.

unfavorable, favorable and irreversible, respectively. As shown in Table S4, when the initial concentrations are $10 \text{ mmol} \cdot \text{L}^{-1}$, the values of adsorption intensity (R_L) lie in ranges of 0–1. Therefore, the present adsorbent (PMA/AC) could be used to the simultaneous removals of Pb(II), Fe (II) and L-Glu from aqueous solutions.

$$R_L = \frac{1}{1 + K_L C} \quad (6)$$

3.2.4. Thermodynamics of adsorption

The thermodynamic parameters such as the Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) for the adsorptions of Pb(II) and Fe(II), L-Glu and L-Thr could be evaluated using the following Eqs. (7) and (8) [15,23]. Where, ΔG^0 : change in free energy ($\text{kJ} \cdot \text{mol}^{-1}$), ΔH^0 : change in enthalpy ($\text{kJ} \cdot \text{mol}^{-1}$), ΔS^0 : change in entropy ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), T : absolute temperature in Kelvin, R : gas constant (8.315×10^{-3}), and K : thermodynamic equilibrium constant. The values of ΔH^0 and ΔS^0 could be calculated from the slope and intercept of the plot of $\ln K$ versus $1/T$. The thermodynamic parameters are summarized in Table S5. Based on the calculated thermodynamic parameters in Table S5, ΔG^0 of negative values indicated that the adsorption for Pb(II), Fe(II), L-Glu and L-Thr on PMA/AC is a feasible and spontaneous process. ΔH^0 of positive values confirmed an endothermic nature process. The ΔH^0 positive values maybe due to the removal of water

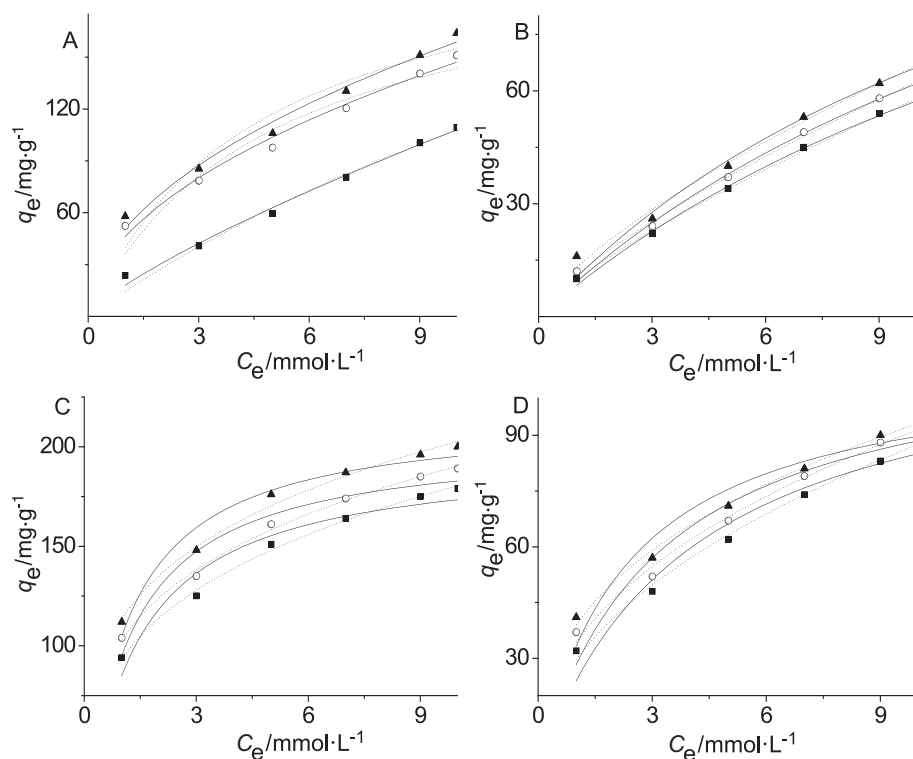


Fig. 7. Adsorption isotherms of Fe(II) (A), Pb(II) (B), L-Thr (C) and L-Glu (D) by PMA/AC at different temperatures. Solid: Langmuir, dash: Freundlich, temperature: 25 °C (■), 35 °C (○), 45 °C (▲).

molecules from the solid–solution interface and the hydrated metal ions [23], and the dehydration process requires energy [24], thus the overall sorption process could be endothermic. The endothermic adsorption process explained above results that the maximum adsorption capacities of Pb(II), Fe(II), L-Glu and L-Thr are increased with the increasing temperature in Table S3. Positive ΔS of adsorption reflected the spontaneity and affinity of the sorbents to Pb(II), Fe(II), L-Glu and L-Thr in Table S5.

$$\Delta G^0 = -2.303RT \lg K \quad (7)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (8)$$

3.2.5. Regeneration of MFT/AC

Regeneration of PMA/AC was investigated by repeated cycle of adsorption/desorption. The desorption was performed in 5 mmol·L⁻¹ EDTA/1 mol·L⁻¹ HNO₃, during 24 h, under stirring, the desorption ratio was calculated from Eq. (9). The amounts of Pb(II) adsorption and recovery percentage from four consecutive adsorption/desorption cycles indicated desorption efficiency as high as 88.3%, and the Pb(II)-free PMA/AC could be reused after neutralization. The corresponding amounts were 90.2% for Fe(II), 89.7% for Pb(II) and 86.3% for L-Glu, respectively.

$$\begin{aligned} \text{Desorption ratio} \\ = (\text{amount of desorbed metal ion} / \text{amount of adsorbed metal ion}) \\ \times 100\% \end{aligned} \quad (9)$$

3.2.6. Selectivity

Since L-Thr could be adsorbed by PMA/AC with a yield loss, PMA/AC formed by molar ratio of ML and L-Asp at 3:1, 2:1 and 1:1 was compared at pH 5.0, 45 °C and 4 h. 10.0 mmol·L⁻¹ L-Thr were introduced in a flask, containing 50 ml solution with a binary mixture of 10.0 mmol·L⁻¹ Pb

(II), Fe(II) or L-Glu due to their coexistence in the fermented crude product of L-Thr. The uptake was conducted continuously till 24 h to attain the equilibrium. 10 ml of the solution was taken then filtrated off, where the residual concentration of L-Thr was determined. The separation factor could be obtained using Eq. (10). Where C_{A1} (C_{B1}) and C_{A2} (C_{B2}) stand for the concentrations of A (B) before and after adsorption, respectively. In the present results, Pb(II), Fe(II) and L-Glu over L-Thr were to be 10.7, 10.8 and 8.4 for 1:1; 18.3, 19.5 and 9.3 for 2:1; 24.6, 19.9 and 10.3 for 3:1, respectively. Therefore, the PMA/AC formed by the molar ratio of 3:1 could be selected. Moreover, the naked AC was used to compare with PMA/AC. Pb(II), Fe(II) and L-Glu over L-Thr were to be 2.7, 1.8 and 1.4, respectively. It is suggested that the present PMA/AC displayed much better selectivity.

$$\text{Separation factor } (S_{A/B}) = (C_{A1} - C_{A2}) \times C_{B2} / [(C_{B1} - C_{B2}) \times C_{A2}] \quad (10)$$

3.3. Application

The present PMA/AC was used to simultaneously remove vestigial Pb(II), Fe(II) and L-Glu from the fermented crude product solution of L-Thr. Based on the above results, the adsorption conditions were performed at pH 5.0, 45 °C and 4 h. In present experiments, the fermented crude product solution of 500 ml 7% L-Thr (pH 5.0) was treated using 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 g PMA/AC, respectively. After the treatment, the solutions were evaporated and crystallized at isoelectric point, then dried at 80 °C to obtain L-Thr product. The relative data were summarized in Table 1. When the dosage is more than 4.0 g PMA/AC (mass rate, L-Thr crude product: PMA/AC = 9:1), the quality of L-Thr could conform the 2015 Quality Standards of Chinese Pharmacopoeia (Quality Standards of Chinese Pharmacopoeia., 2015)[22]. Meanwhile, it is notable that As (III) could be simultaneously removed too in the processes (here the uptake behaviors did not be shown). Therefore, 4 g PMA/AC

Table 1

Treatment effect of the fermented crude product solution of 500 ml 7% L-Thr depending on the quantity of PMA/AC

	Fe (II)/ $\mu\text{g}\cdot\text{g}^{-1}$	Pb(II)/ $\mu\text{g}\cdot\text{g}^{-1}$	As/ $\mu\text{g}\cdot\text{g}^{-1}$	L-Glu/wt%	L-Thr/wt%
Original	18.90	10.63	1.47	3.2	96.05
Standards	≤ 10.00	≤ 10.00	≤ 1.00	default	≥ 98.5
2 g PMA/AC	5.43	3.13	0.46	1.48	98.02
3 g PMA/AC	3.25	2.66	0.33	1.08	98.43
4 g PMA/AC	2.65	2.11	0.25	0.85	98.67
5 g PMA/AC	2.11	1.85	0.20	0.64	98.89
6 g PMA/AC	1.81	1.62	0.18	0.53	99.01
7 g PMA/AC	1.63	1.54	0.16	0.46	99.09

could be used for refining 500 ml 7% L-Thr fermented crude product solution.

To investigate the adsorption, XPS experiment was done. Fig. 8 shows the XPS of PMA/AC before (a), after getting immersed in 30 ml $10\text{ mmol}\cdot\text{L}^{-1}$ mix solution of Pb^{2+} and Fe^{2+} (b), 30 ml $10\text{ mmol}\cdot\text{L}^{-1}$ crude L-Thr solution (c) at pH 5.0, 45°C and 4 h. For curve a, the peaks at 285.1 eV and 533.1 eV match to C1s and O1s. A very small peak at 398.3 eV could be assigned to N1s due to the existence of N functional group at PMA/AC. After the adsorption in the mix solution (b) of Pb (II) and Fe(II), two new peaks at 139 eV and 710 eV could be seen corresponding to the Pb4f and Fe2p, respectively, suggesting the effective absorption. After the adsorption in the crude L-Thr solution (c), the peaks at 398.3 eV (N1s) are obviously strong, applying the adsorption of PMA/AC to amino acid too. But there are no any heavy metal peaks; the reason probably relates that the contents of Pb(II) or Fe(II) in the real sample are too low to detect using XPS technique. The conjecture was proven by the ICP experiment, the data were summarized in Table 1, you can see that the content of heavy metals obviously decreased after the treatment using PMA/AC.

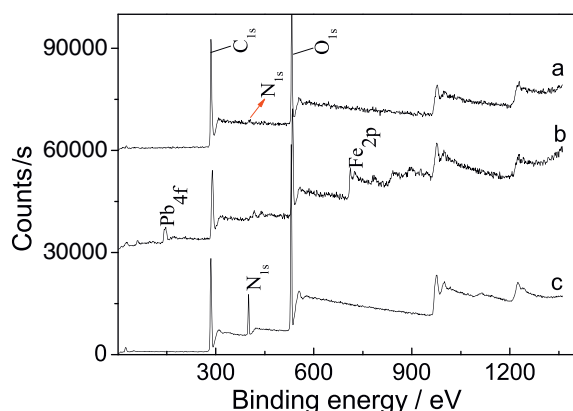


Fig. 8. XPS of PMA/AC before (a), and after getting immersed in 30 ml $10\text{ mmol}\cdot\text{L}^{-1}$ mix solution of Pb^{2+} and Fe^{2+} (b), 30 ml $10\text{ mmol}\cdot\text{L}^{-1}$ crude L-Thr solution (c) at pH 5.0, 45°C and 4 h.

4. Conclusions

L-aspartic acid melamine resin grafted-activated carbon (PMA/AC) was obtained by a pressure relief-dipping-microwave assisted synthesis method. The adsorption behaviors of Pb(II), Fe(II) and L-Glu at PMA/AC show good correlation with pseudo-second-order model, and the adsorptions are feasible, spontaneous and endothermic. The vestigial Pb

(II), Fe(II) and L-Glu could be simultaneously removed using PMA/AC from the fermented crude product solution of 7% L-Thr (mass rate = 9:1) at pH 5.0, 45°C with 4 h. This work provides a very efficient and convenient approach for exploring promising PMA/AC composite to refining the fermented crude product of L-Thr.

Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2017.12.013>.

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