A novel fabrication of monodisperse melamine-formaldehyde resin microspheres to adsorb lead (II)

Guangtian Ming, Hongdong Duan, Xia Meng, Guangming Sun, Wenjun Sun, Yu Liu, Lucian Lucia

PII: S1385-8947(15)01664-2
DOI: http://dx.doi.org/10.1016/j.cej.2015.12.007
Reference: CEJ 14510

To appear in: *Chemical Engineering Journal*

Received Date: 17 July 2015
Revised Date: 4 November 2015
Accepted Date: 1 December 2015

Please cite this article as: G. Ming, H. Duan, X. Meng, G. Sun, W. Sun, Y. Liu, L. Lucia, A novel fabrication of monodisperse melamine-formaldehyde resin microspheres to adsorb lead (II), *Chemical Engineering Journal* (2015), doi: http://dx.doi.org/10.1016/j.cej.2015.12.007

A novel fabrication of monodisperse melamine-formaldehyde resin microspheres to adsorb lead (II)

Guangtian Ming[a], *Hongdong Duan*[a,*], *Xia Meng*[a], *Guangming Sun*[b], *Wenjun Sun*[b], *Yu Liu*[c], *Lucian Lucia*[c]

[a] *School of Chemistry and Pharmaceutical Engineering, Qilu University of Technology, Jinan 250353, PR China*

[b] *Shandong Qilu Paint Industry Company, Liaocheng 252042, PR China*

[c] *Key Lab of Pulp & Paper Science and Technology, Qilu University of Technology, Ministry of Education, Jinan 250353, PR China*

E-mail: hdduan67@gmail.com

Abstract

Monodisperse melamine-formaldehyde (MF) resin microspheres were prepared by dilute solution precipitation polymerization without any surfactant and stabilizer. The optimal preparation conditions and the mechanism of microsphere formation of the microspheres were investigated by microscopy, Fourier transform infrared spectra, thermal stability, and particle size analysis. The microspheres prepared under optimal conditions had a clean surface, good thermal stability, and a narrow distribution with a mean diameter of about 2.5 μm. In addition, the microsphere had an abundance of amino and imino functional groups that could supply numerous active points for adsorption. From a study of the static and dynamic adsorption of lead (II) (Pb (II)) using MF resin microspheres as the adsorbent, it was found that the resin microspheres showed a fast adsorption and high removal efficiency of Pb (II).

Key words: *melamine-formaldehyde resin microspheres, fabrication, amino and imino, adsorption, lead (II)*

1. Introduction

Resin microspheres are a polymeric material that have been widely used as a catalyst support [1], drug carrier [2], absorption material [3-5], carbon matrix [6, 7] and template [8]. There are many preparation methods for resin microspheres [9] including suspension polymerization [10], emulsion polymerization [11, 12], dispersion polymerization [13, 14], and precipitation polymerization [2, 15] that are employed for specific end uses.

Generally, to obtain smaller size microspheres and prevent agglomeration, most researchers adjusted the type and dosage of surfactants and stabilizers during their preparation. Cheong et al. [16] prepared monodisperse MF resin microspheres (~ 500 nm) at 85°C with Gum Arabic and sodium lauryl sulfate as surfactant and stabilizer. Such preparation materials are generally very difficult to remove during subsequent processing. It can prevent grafting on the surface and thus limit their applications.

Thus, a novel synthetic method has been adopted to overcome the latter difficulties that takes advantage of the good solubility of melamine and formaldehyde to provide a high degree of polymerization MF resin. This resin increases the surface tension of water and gradually precipitates from aqueous solutions without surfactants. Ma et al. [17] prepared MF microspheres in an aqueous phase having ~ 5 μm diameters without surfactants. Although the approach benefited from a green perspective, the microspheres were prepared under high reaction temperatures giving an inhomogeneous diameter distribution. Furthermore, the heating caused the microspheres to lose numerous amino and imino groups that are essential for many final applications.

To develop uniform microspheres in a green manner that does not suffer from loss of critical functional groups (*vide supra*), a simple and convenient synthetic method without surfactant and stabilizer was adopted and is herein described. The effects of the reactant molar ratio, reaction time, reaction temperature, mass ratio of raw materials relative to water and the mechanism of sphere formation and growth were determined by SEM, TGA, FTIR and particle size analysis. The melamine resin microspheres showed high efficiency as sorbents for the static and dynamic adsorption of Pb (II) and provided equilibrium, kinetics and isotherm data.

2. Experimental

2.1. Materials

Melamine and formaldehyde (37 wt-%) of analytical reagent grade were obtained from Tianjin DaMao Chemical Reagent Factory, Tianjin, China. Analytical reagent grade reagents including $Pb(NO_3)_2$, CH_3COONa, CH_3COOH, disodium hydrogen phosphate dehydrate and sodium phosphate dibasic dodecahydrate were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were used without further purification.

2.2. Fabrication of MF resin microspheres

2.2.1. Effect of reactant molar ratio

Distilled water (300 mL) was added into a 500 mL four-neck round bottomed glass reactor and heated to 70°C under stirring. Next, 15 g of formaldehyde solution (37 wt-%) was added until the temperature reached 80°C. Afterwards, either 3.0 g, 6.0 g, 7.5 g, 11.5 g of melamine was added. The system was stirred over 1 h at rate of 200 r/min, and the MF resin microspheres solution was placed into 1000 mL beaker. Next, 500 g of distilled water was added rapidly. The solution was continuously stirred until the MF resin microspheres solution cooled down to room temperature. After the process of standing and layering, the lower turbid solution was collected and centrifuged three times. The MF resin microspheres were dried at room temperature and further dried in vacuum oven at 80°C for 10 h. The MF resin microspheres were obtained through air cooling and pulverization by an agate mortar.

2.2.2. Effect of reaction time

Distilled water (300 mL) was added into a 500 mL four-neck round bottomed glass reactor and heated to 70°C under stirring. Next, 15 g of formaldehyde solution (37 wt-%) was added until the temperature reached 80°C. Then 6.0 g of melamine was added after the temperature was reached at a stirring rate of 200 r/min for 10 min, 30 min, 60 min, 90 min, 120 min, respectively. The same post-treatment of samples introduced in Section **2.2.1** was used here to obtain the final product.

2.2.3. Effect of reaction temperature

Distilled water (300 mL) was added into a 500 mL four-neck round bottomed glass reactor and heated to 65°C, 70°C, 75°C, 80°C, 85°C under stirring, respectively. Next, 15 g of formaldehyde solution (37 wt-%) was added into the mixture that was heated at 80°C. Afterwards, 6.0 g of melamine was added into the solution with a stirring rate of 200 r/min for 1 h. The treatment of samples was similar to that in Section **2.2.1**.

2.2.4. Effect of mass ratio of raw materials and water

Distilled water (50, 100, 200, 300, 400 mL) was added into a 500 mL four-neck round bottomed glass reactor and heated to 70°C under stirring. Then 15 g of formaldehyde solution (37 wt-%) was added and the system was raised to 80°C. Afterwards, 6.0 g of melamine was added into the solution at a stirring rate of 200 r/min for 1 h. The treatment of samples was similar to that in Section **2.2.1**.

2.3. Characterization

The morphology of MF resin microspheres was examined by scanning electron microscopy (SEM) (Hitachi S-70) where the samples were treated by spray-gold before observation. Fourier transform infrared spectra (FTIR) were recorded on a Nicolet NEXUS-550 FTIR spectrometer with KBr powder in the range of 4000-500 cm^{-1}. Thermogravimetric analysis (TGA) of the MF resin microspheres was performed on a SDT-Q600 instrument under N_2 with a heating rate of 10°C min^{-1}. Average particle size and size distribution were determined by Malvern Zetasizer Nano ZS90.

2.4. Batch adsorption experiments

Stock solutions of 1000 mg/L were prepared by dissolving 1 g of Pb (II) nitrate in 1000 mL distilled water. Different concentrations (20, 50, 100, 200, 300 and 500 mg/L) of Pb (II) were prepared by further dilution from the stock solution. Buffer solutions ranging from pH 4.0 to pH 8.0 were prepared from 0.5 mol/L sodium acetate and 0.5 mol/L acetic acid (HAc–NaAc). Alkaline buffers solutions were prepared from 0.5 mol/L disodium hydrogen phosphate dihydrate and 0.5 mol/L sodium phosphate dibasic dodecahydrate. The concentrations of Pb (II) were determined by inductively coupled plasma mass spectrometry (ICP-MS). The adsorption capacity (Q_e) of Pb (II) on MF resin microspheres was calculated as follows [18, 19]:

$$Q_e = \frac{(C_0 - C_e)V}{M} \tag{1}$$

where C_0 (mg/mL) is the initial concentrations of Pb (II), C_e (mg/mL) is the concentration of Pb (II) reached the adsorption equilibrium, V (mL) is the solution volume, and M (g) is the amount of the microspheres [20].

2.4.1. Effect of the pH value on Pb (II) adsorption

Approximately 2 g of MF resin microspheres was placed into 250 mL conical flasks along with 100 mL of Pb (II) ion solution with a concentration of 100 mg/L, 10 mL buffer solution (pH = 4, 5, 6, 7 and 8), respectively. The mixture was shaken in a constant temperature bath shaker (100 rpm) at 25°C. After adsorption equilibrium, the solids were filtered. The concentrations of Pb (II) were determined by ICP-MS.

2.4.2. Kinetics

Approximately 2 g of MF resin microspheres was placed in 250 mL conical flasks, to which was added 100 mL of Pb (II) solution at concentrations of 30, 50 and 100 mg/L, that were buffered at optimum pH (pH = 7); the mixture was shaken at a speed of 100 rpm and a constant temperature of 25°C. The samples were collected at preset intervals and the upper layer liquid was taken out until adsorption equilibrium was reached. After the adsorption equilibrium, the microspheres were filtered and the filtrate was diluted to 10 mL. Concentrations of Pb (II) were determined as above.

2.4.3. Isotherms and thermodynamics

MF resin microspheres (2 g) was placed into 250 mL conical flasks, to which was added 10 mL buffer solution (pH = 7), 100 mL Pb (II) solution at concentrations of 20, 50, 100, 200, 300 and 500 mg/L, respectively. The mixtures were shaken in a shaker (25°C, 30°C and 35°C) at a speed of 100 rpm. The samples were collected at preset time intervals. The upper layer liquid was taken out until adsorption equilibrium was reached. Afterwards, the solids were filtered and the filtrate was diluted to 10 mL. The concentrations of Pb (II) were determined as above.

2.4.4. Batch desorption

The solids were filtered and washed thoroughly with distilled water. The adsorbed Pb (II) ions were desorbed by HCl in different concentrations for 24 h at room temperature under constant shaking in a constant temperature bath shaker. The final concentrations of Pb (II) were determined by ICP-MS. The percentage of desorption was calculated by the following expression:

$$\text{Desorption (\%)} = \frac{\text{Amount of metal ion desorbed to the elution medium}}{\text{Amount of metal ion sorbed on MF resin microspheres}} \times 100\% \qquad (2)$$

2.5. Column adsorption and desorption experiments

Approximately 7 g of MF resin microspheres was placed in a stationary glass column (3 cm i.d. × 30 cm length). A glass wool plug was provided at the bottom to support the adsorbent bed and prevent removal of adsorbent. The Pb (II) solution at a concentration of 100 mg/L, buffer solution (pH = 7) with a flow rate 1 mL/min was passed continuously through the stationary bed of adsorbent. The samples were collected at different time intervals in the bottom of the column and the concentrations of Pb (II) were determined via ICP-MS from which the dynamics adsorption curve was measured.

Hydrochloric acid solution with a concentration of 0.1 mol/L was used as the eluting agent at 2 mL/min flow rate. The aqueous samples were collected at the different time intervals and the concentrations of Pb (II) were similarly analyzed.

The performance of column is described by the concept of breakthrough curve. The breakthrough curve can be expressed as the plot of C_t/C_0 (where C_t is the outlet Pb (II) concentration and C_0 is the inlet Pb (II) concentration) versus time or volume of the effluent. Total adsorbed Pb (II) quantity (q_{total}; mg), in the column for a specific initial concentration and flow rate can be calculated from Equation (3):

$$q_{total} = \frac{Q}{1000}\int_{t_0}^{t_{total}} C_{ad}\, dt = \frac{Q}{1000}\int_{t_0}^{t_{total}} (C_0 - C_t)\, dt \quad (3)$$

where Q is the volumetric flow rate (mL/min), C_{ad} is the adsorbed Pb (II) concentration (mg/L), t_{total} is the total time of flow (min) [21], respectively.

2.6. Regeneration

The regenerated adsorbents were washed with deionized water repeatedly and further dried in vacuum oven at 80°C for 10 h. To test the reusability of the MF resin microspheres, a total of six (6) repeats of the adsorption-desorption cycle were done.

3. Results and discussion

3.1. Synthesis of MF resin microspheres

Fig. 1 is the SEM images of MF resin microspheres that shows four different samples prepared with a different molar ratio of formaldehyde relative to melamine. It can be clearly seen that the molar ratio of formaldehyde versus melamine has a great influence on formation, smoothness, and dispersion of these microspheres. When the molar ratio of formaldehyde relative to melamine was 2:1 (Fig. 1(a)), the surface was rough likely because the polymerization degree of the resin and the surface tension of water both were seriously non-uniform, leading to a high quantity of linear melamine resin that adhered to the surface of the microsphere. These linear melamine resins were attributed to a reduced frequency of collisions between melamine and formaldehyde and thus could not interact sufficiently to produce a polymer with high surface tension. Therefore a high concentration of resins with irregular shapes adhered to the surface of the microspheres. As can be seen in Fig. 1(b), the smoothness increased with an increasing level of formaldehyde, but when the molar ratio was ~ 5:1 (Fig. 1(d)), the samples showed significant aggregation. Theoretically, one melamine molecule could react with six formaldehyde molecules. A high molar ratio of formaldehyde versus melamine thus increased the reaction rate and degree of polymerization, promoting precipitation of resin microspheres. The precipitated resin microspheres had a very high local concentration of active methylol groups on their surface which could crosslink and etherify at high temperature conditions without acidification, leading to tremendous aggregation. The aggregated resin microspheres were very difficult to separate by most common means. When the molar ratio was 4:1 (Fig. 1(c)), the melamine resin microspheres showed perfect formation, clean surface, outstanding dispersion, and uniform size.

Fig. 2 is the SEM images of MF resin microspheres prepared at different reaction times. It can be clearly seen that with more reaction time, the size and smoothness of MF resin microspheres increased. However, the size did not change after 60 min. It is to provide possible from these images a postulate for the growth mechanism. At the beginning of the reaction, higher monomer concentrations increase the reaction rate because of a high degree of polymerization, after which a large number of smaller size microspheres particles precipitated. As shown in Fig. 2(a), when the reaction time reached 10 minutes, a large quantity of microspheres having non-uniform size agglomerated. As shown in Fig. 2(b), with reaction time increasing, small microspheres agglomerated into big microspheres. Therefore, the number of small size microspheres gradually decreased with a concomitant increase in bigger microspheres. Yet, when the reaction time was too long, the number of monomers, concentrations and reaction speed decreased. The low polymerization degree linear melamine resin with a large number of active methylol easily adhered to the surface of the microspheres as shown in Fig. 2(d, e). When the reaction time was 60 min, the melamine-resin microspheres exhibited uniform size and high smoothness as shown in Fig. 2(c). In conclusion, the growth mechanism of the melamine microspheres was likely uncovered: a large number of smaller microspheres are generated that tend to react with each other to form larger size microspheres. A linear resin with a low degree of polymerization was able to graft onto the microsphere surface.

Fig. 3 shows the SEM images of MF resin microspheres prepared from five different reaction temperatures. From these images, it could be clearly seen that, at higher temperature, the size becomes smaller and the surface of microspheres is smoother. However, smoothness could not change much after 80°C. High temperature leads to fast reaction rate producing resins with a high polymerization degree in a short precipitation time. At higher temperatures, the kinetics of agglomeration of smaller microspheres decreased because of the quick resin producing process. The fast reaction rate resulted in low concentration monomers which were hardly able to lead to a high polymerization degree at high temperature instead of precipitation in the form of microspheres. In addition, the low degree of polymerization linear resin was unable to efficiently coat the surface of the microspheres. Thus, the microspheres solidified more quickly at high temperatures, while the surface still contained a small amount of reactive functional groups. Thus, linear resins were harder to crosslink and etherify. This meant that smaller microspheres needed to be prepared at high temperatures. When the reaction temperature was 80°C, the melamine resin microspheres exhibited better morphologies as shown in Fig. 3(d).

Fig. 4 is the SEM images of MF resin microspheres prepared at five different mass ratios of raw materials relative to water. These samples exhibited reduced agglomeration, better dispersion, and uniform size with increasing the relative ratio of water. However, monodispersity and uniformity changed little after the mass ratio of raw materials relative to water was 1:26. More of the water resulted in bigger spaces between the microspheres which decreased the highly sought collision probability of microspheres. In addition, a small relative mass ratio of water increased the initial concentration of the reactants. Because the same reaction temperature and stirring speed were controlled, the surface was uncompleted. The microspheres contained a high amount of active functional groups and highly cross-linking resin in the case of less water. With the relative molecular mass of water increasing, the concentrations of the reactants and reaction speed decreased. When the mass ratio of raw materials relative to water was 1:26, the melamine resin microspheres exhibited more uniform size and better dispersion as shown in Fig. 4(d).

The optimum experimental conditions were used for Pb (II) adsorption experiments, in which the molar ratio of formaldehyde relative to melamine was 4:1, 60 min, 80°C and the mass ratio of raw materials relative to water was 1:26.

3.2. Characterization of MF resin microspheres

The Fourier transform infrared spectra (FTIR) of MF resin microspheres before and after Pb (II) adsorption (Fig. 5) were recorded in the range of 4000 to 500 cm^{-1}. The FTIR spectrum of MF resin microspheres before adsorption is shown in Fig.5 (a); the peaks associated with amino (-NH$_2$) and imino (-NH-) stretching was found at 3325 cm^{-1}, methylene (-CH$_2$-) stretching was found at 1489 cm^{-1} and 1165 cm^{-1}, and 1, 3, 5-s-triazing ring mode at 1558 cm^{-1} and 812 cm^{-1} [22]. The spectrum of MF resin microspheres after adsorption is shown in Fig.5 (b). It is found that the characteristic sorption peaks of the -NH$_2$ and -NH- shift from 3325 cm^{-1} to 3334 cm^{-1} which indicates the main role of -NH$_2$ and -NH- groups in the improved adsorption phenomenon of Pb (II). The results of FTIR analysis indicated the presence of the characteristic absorption peak of the microspheres.

The result of the thermal gravimetric analysis (TGA) of MF resin microspheres is shown in Fig. 6. The initial major weight loss between 140-260°C can be attributed to the free formaldehyde molecules and evaporation of water; interestingly, the structure of the MF resin microspheres did not change. The substantial weight lost rapidly at temperatures between 400-800°C because the samples decomposed into carbon residue. It can be concluded that the MF resin microspheres had good thermal stability, which could be ascribed the stable triazine groups.

The particle size distribution of MF resin microspheres were obtained by particle size analysis. Size measurement was repeated 3 times for each sample and relative standard deviations were less than 5%. Average particle sizes of the MF resin microspheres with varying process variables are listed in Table 1.

3.3. Influence of pH on adsorption

The pH of the aqueous solution is one of the most important factors in adsorption processes [23, 24]. The concentration of Pb (II) was examined over the pH range of 4-8 at 298 K. Fig. 7 (a) shows the influence of pH on the adsorption process, showing that the highest equilibrium adsorption was achieved at pH of 7.0.

This phenomenon may be explained from several aspects. It could be attributed to the amino groups (-NH$_2$) and imino groups (-NH-) within the MF resin microspheres that acted as the active adsorbents for metal ion adsorption. The zeta potential of MF resin microspheres as a function of pH was shown in Fig. 7 (b). At lower pH values, a relatively high concentration of H$^+$ competed with Pb (II) as the active sites during the adsorption process. The protonation of the amino and imino groups would lead to a strong electrostatic repulsion for absorption between them and the Pb (II) ions. Therefore, the adsorption capacity of MF resin microspheres for Pb (II) is low. As pH increased, protonation became slower, while the competition of the protons with the Pb (II) ions for the active sites became less significant. Thus, more Pb (II) ions are bound with active functional groups on the surface of MF resin microspheres [25]. The adsorption plateau value of the Pb (II) was achieved at pH 7.0 for subsequent experiments.

3.4. Adsorption kinetics

To further study the kinetics of the adsorption, two most widely applied kinetic models, i.e., the Lagergren pseudo-first-order [26] and pseudo-second-order [27] equation can be used to fit the adsorption data, just as shown in the following [28, 29]:

$$\log(Q_e - Q_t) = \log Q_e - \frac{tk_1}{2.303} \quad (4)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{5}$$

where Q_e (mg/g) and Q_t (mg/g) are the amounts of Pb (II) adsorbed at equilibrium and time t (min); k_1 (min^{-1}) is the Lagergren pseudo-first-order rate constant of adsorption, k_2 (g min^{-1} mg^{-1}) is the pseudo-second-order rate constant of adsorption [30].

Fig. 8 shows the effects of contact time on the adsorption capacity of Pb (II) ions onto MF resin microspheres at different initial concentrations (30, 50, 100 mg/L). The adsorption capacity increased rapidly in the first 20 min and then tended to equilibrium which showed that the adsorption process is fast and the efficiency of adsorption is higher.

The Lagergren pseudo-first-order and pseudo-second-order data fitting results were shown in Fig. 9 and Table 2. It is obvious that the adsorption of Pb (II) on MF resin microspheres followed better correlation coefficient by pseudo-second-order kinetics model [27, 31].

Compared with other reported adsorbents, MF resin microspheres had many advantages, including cheap materials, simple synthesis method, fast adsorption process, and easy industrialization. First, the raw materials for the adsorption of MF resin microspheres are inexpensive and readily available. Secondly, the adsorbent preparation is also simple and will not lead to secondary pollution. Although not as effective as a commercial chelating resin [3] for adsorbing Pb (II), this is more than offset by the low cost and high availability of adsorbents considered. In terms of adsorption rate, there is little difference between guanidine-modified hydrogels [32] and MF resin microspheres. However, the high cost and complicated preparation technology of guanidine-modified hydrogels makes its application difficult. On the other hand, the adsorption rate of the MF resin microspheres was faster than the low-cost adsorbents [33] and the adsorption performance of MF resin microspheres was superior to porous resins [25] and Dowex 50W synthetic resin [34].

3.5. Adsorption isotherms

Adsorption isotherms describe the relationship between equilibrium absorption capacity and concentration at certain temperature. Fig. 10 represents the adsorption isotherms of MF resin microspheres for Pb (II) at 298 K, 303 K and 308 K.

The linear forms of the Langmuir [35] and Freundlich [36] isotherms are represented by the following equations:

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{bQ_m}\frac{1}{C_e} \tag{6}$$

$$\log Q_e = \log K_F + \frac{1}{n}\log C_e \tag{7}$$

where Q_e (mg/g) is the equilibrium Pb (II) concentration on the adsorbent, C_e (mg/L) is the equilibrium Pb (II) concentration in solution, Q_m (mg/g) is the amount of Pb (II) at maximum monolayer, and b is Langmuir adsorption constant, K_F and 1/n are Freundlich constants corresponding to adsorption capacity and adsorption intensity [37, 38], respectively.

Fig. 11 shows the fitting plots of Langmuir and Freundlich adsorption isotherms of Pb (II) on MF resin microspheres at 298 K (plots at 303 K and 308 K not shown). The Langmuir and Freundlich data fitting results are shown in Table 3. It is obvious that the adsorption of Pb (II) on MF resin microspheres had a superior correlation coefficient using the Langmuir model, while the adsorption of

Pb (II) on MF resin microspheres could be modeled by a monolayer adsorption process [39].

3.6. Thermodynamic parameters

Thermodynamics parameters including Gibbs free energy change (△G), enthalpy change (△H), and entropy changes (△S) [33, 37] were calculated by the following equations:

$$\Delta G = -RT \ln K_L \tag{8}$$

$$\ln K_L = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{9}$$

where T and R represent the system temperature (K) and the universal gas constant (8.314 J/mol K). K_L is the sorption equilibrium constant determined from the slope of ln (Q_e/C_e) against C_e at different temperatures and extrapolating to zero C_e. The values of △H and △S were obtained from the slope and intercept of the Vant Hoff plot of ln K_L against 1/T (Fig. 12).

The results were tabulated in Table 4. The negative value of △H and △S indicated the exothermic nature of the sorption process and spontaneity at low temperatures. The negative values of △G confirmed the spontaneity and feasibility of the adsorption process. So the adsorption is a chemical adsorption.

3.7. Batch desorption

To reduce costs and regenerate adsorbents, the adsorbent desorption performance should be investigated to optimize it [40]. From Fig. 13, it can be seen that 0.5 mol/L HCl provided a higher desorption ratio and more than 95% of the adsorbed Pb (II) ions could be easily removed from the microspheres. These results indicate that MF resin microspheres could be easily regenerated.

3.8. Dynamic adsorption and desorption

The adsorption study by the dynamic method was chosen due to some operational advantages [21, 41-44]. The breakthrough curve can be expressed by plotting the concentration C_e/C_0 (where C_e is the outlet Pb (II) concentration and C_0 is the inlet Pb (II) concentration) versus time or volume of the effluent [45]. The dynamic adsorption curve of MF resin microspheres for Pb (II) is shown in Fig. 14. Dynamic adsorption experiments were performed on MF resin microspheres at an initial concentration of Pb (II) of 100 mg/L and flow rate = 1 mL/min. It could be seen from Fig. 14 that the breakthrough point of adsorption was 60 min. During 0 ~ 60 min stage, the Pb (II) was almost entirely adsorbed. These results indicate that the dynamic adsorption reached equilibrium after 60 min. The dynamic adsorption capacity for Pb (II) was 6.15 mg/g that indicates that the solute uptake is quicker and efficiency of sorption is higher.

Outstanding desorption performance of an adsorbent is important in its potential practical applications. The dynamic desorption curve of MF resin microspheres for Pb (II) ions was shown in Fig. 15. It can be seen that at 40 min, the MF resin microspheres desorbed completely which indicates that the MF resin microspheres had outstanding elution properties [45, 46].

3.9. Regeneration studies

The regeneration of adsorbents is an important factor for an effective absorption material. The adsorption-desorption cycle of the MF resin microspheres was shown in Fig. 16. The results clearly show that the MF resin microspheres could be easily regenerated without significantly compromising its adsorption capacity. Therefore, the MF resin microsphere adsorbent had excellent reusability.

4. Conclusions

Monodisperse melamine resin microspheres have been successfully synthesized without any surfactant, emulsifier, or dispersant. The effects of the reactant molar ratio, reaction time, reaction temperature, mass ratio of raw materials relative water were investigated. When the molar ratio of formaldehyde relative melamine was 4:1, MF resin microspheres expressed clean surfaces and good size uniformity. With increasing reaction time and temperature, the surface became smooth. When the reaction time was 60 min and the reaction temperature was 80°C, the smoothness did not change. The growth mechanism of the melamine microspheres was hypothesized to consist of the following: numerous smaller microspheres were generated, then reacted with each other to form larger size microspheres. Linear resin with a low degree of polymerization merged onto microsphere surface. With the relative ratio of water increasing, the monodispersity and uniformity were better. However, monodispersity and uniformity did not change after the mass ratio of raw materials relative to water was 1:26. Therefore, monodisperse melamine-formaldehyde resin microspheres with clean surface were able to be prepared. The microsphere prepared under an optimal condition showed good thermal stability and a narrow distribution with a mean diameter of about 2.5 μm. The MF resin microspheres had higher adsorption rate and could be used repeatedly. The maximum capacity of the column was found to be about 6.15 mg/g for Pb (II) of MF resin microspheres. The adsorption process followed an Langmuir isotherm and pseudo-second-order kinetics model. Kinetics and thermodynamic studies indicated that the adsorption process was an exothermic and spontaneous reaction and the adsorption reaction is a chemical adsorption. Furthermore, numerous active functional groups, such as amino and imino, were on the surface of MF resin microspheres, endowing them with great potential applications in the adsorption metal ions.

Acknowledgement

This work was supported by the National Science Foundation of China (Grant No. 31270626) and the Project of Shandong Province Science and Technology Development Plan (Grant No. 2014GGX102023).

References

[1] Y. Wang, Y. Li, S. Liu, B. Li, Fabrication of chitin microspheres and their multipurpose application as catalyst support and adsorbent, Carbohydrate polymers 120 (2015) 53-59.

[2] W. Lu, C. Qian, L. Bi, L. Tao, J. Ge, J. Dong, W. Qian, Biomolecule-based formaldehyde resin microspheres loaded with Au nanoparticles: a novel immunoassay for detection of tumor markers in human serum, Biosensors & bioelectronics 53 (2014) 346-354.

[3] A. Agrawal, K.K. Sahu, Separation and recovery of lead from a mixture of some heavy metals using Amberlite IRC 718 chelating resin, Journal of hazardous materials 133 (2006) 299-303.

[4] S. Wang, K. Wang, C. Dai, H. Shi, J. Li, Adsorption of Pb^{2+} on amino-functionalized core–shell magnetic mesoporous SBA-15 silica composite, Chemical Engineering Journal 262 (2015) 897-903.

[5] X. Zhou, Y. Su, S. Zhao, Preparation of Chitosan-Quercetin Resin Microspheres and its Adsorption Properties for Flavonoids, Separation Science and Technology 48 (2013) 941-946.

[6] M. Li, Y. Zhang, L. Yang, Y. Liu, J. Yao, Hollow melamine resin-based carbon spheres/graphene composite with excellent performance for supercapacitors, Electrochimica Acta 166 (2015) 310-319.

[7] S. Ren, M. Wang, C. Jia, C. Hao, X. Wang, Fabrication of Supercapacitors using Carbon Microspheres Synthesized from Resorcinol-Formaldehyde Resin, Energy Technology 1 (2013) 332-337.

[8] H. Liu, H. Li, Z. Ding, A. Fu, H. wang, P. Guo, J. Yu, C. Wang, X.S. Zhao, Preparation of Porous Hollow SiO_2 Spheres by a Modified Stöber Process Using MF Microspheres as Templates, Journal of Cluster Science 23 (2011) 273-285.

[9] R. Arshady, Suspension, emulsion, and dispersion polymerization: A methodological survey, Colloid and Polymer Science 270 (1992) 717-732.

[10] C. Dhiwar, A. Tiwari, A.K. Bajpai, Nano-iron oxide-encapsulated chitosan microspheres as novel adsorbent for removal of Ni (II) ions from aqueous solution, Research on Chemical Intermediates 39 (2012) 2989-3009.

[11] D. Wang, M. Chen, C. Wang, J. Bai, J. Zheng, Synthesis of carbon microspheres from urea formaldehyde resin, Materials Letters 65 (2011) 1069-1072.

[12] Y. Yang, X. Liu, M. Guo, S. Li, W. Liu, B. Xu, Molecularly imprinted polymer on carbon microsphere surfaces for adsorbing dibenzothiophene, Colloids and Surfaces A: Physicochemical and Engineering Aspects 377 (2011) 379-385.

[13] R. Razali, A.K. Zak, W.H.A. Majid, M. Darroudi, Solvothermal synthesis of microsphere ZnO nanostructures in DEA media, Ceramics International 37 (2011) 3657-3663.

[14] Y. Wu, Y. Li, J. Xu, D. Wu, Incorporating fluorescent dyes into monodisperse melamine–formaldehyde resin microspheres via an organic sol–gel process: a pre-polymer doping strategy, Journal of Materials Chemistry B 2 (2014) 5837.

[15] H. Zhou, S. Xu, H. Su, M. Wang, W. Qiao, L. Ling, D. Long, Facile preparation and ultra-microporous structure of melamine-resorcinol-formaldehyde polymeric microspheres, Chemical communications 49 (2013) 3763-3765.

[16] I.W. Cheong, J.S. Shin, J.H. Kim, S.J. Lee, Preparation of monodisperse melamine-formaldehyde microspheres via dispersed polycondensation, Macromolecular Research 12 (2004) 225-232.

[17] F. Ma, H. Zhao, L. Sun, Q. Li, L. Huo, T. Xia, S. Gao, G. Pang, Z. Shi, S. Feng, A facile route for nitrogen-doped hollow graphitic carbon spheres with superior performance in supercapacitors, Journal of Materials Chemistry 22 (2012) 13464.

[18] X. Chen, K.F. Lam, K.L. Yeung, Selective removal of chromium from different aqueous systems using magnetic MCM-41 nanosorbents, Chemical Engineering Journal 172 (2011) 728-734.

[19] X. Jing, F. Liu, X. Yang, P. Ling, L. Li, C. Long, A. Li, Adsorption performances and mechanisms of the newly synthesized N,N'-di (carboxymethyl) dithiocarbamate chelating resin toward divalent heavy metal ions from aqueous media, Journal of hazardous materials 167 (2009) 589-596.

[20] T. Wang, S. Lu, Q. Xia, Z. Fang, S. Johnson, Separation and purification of amygdalin from

thinned bayberry kernels by macroporous adsorption resins, Journal of chromatography. B, Analytical technologies in the biomedical and life sciences 975 (2015) 52-58.

[21] P. Agrawal, A.K. Bajpai, Dynamic Column Adsorption Studies of Toxic Cr(VI) Ions onto Iron Oxide Loaded Gelatin Nanoparticles, Journal of Dispersion Science and Technology 32 (2011) 1353-1362.

[22] Y. Wu, Y. Li, L. Qin, F. Yang, D. Wu, Monodispersed or narrow-dispersed melamine–formaldehyde resin polymer colloidal spheres: preparation, size-control, modification, bioconjugation and particle formation mechanism, J. Mater. Chem. B 1 (2013) 204-212.

[23] K.F. Lam, C.M. Fong, K.L. Yeung, Separation of precious metals using selective mesoporous adsorbents, Gold Bulletin 40 (2007) 192-198.

[24] V.C. Taty-Costodes, H. Fauduet, C. Porte, A. Delacroix, Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of Pinus sylvestris, Journal of hazardous materials 105 (2003) 121-142.

[25] C. Li, H. Duan, X. Wang, X. Meng, D. Qin, Fabrication of porous resins via solubility differences for adsorption of cadmium (II), Chemical Engineering Journal 262 (2015) 250-259.

[26] Y.S. Ho, G. McKay, The sorption of lead(II) ions on peat, Water research 33 (1999) 578-584.

[27] Y.S. Ho, J.C.Y. Ng, G. McKay, Removal of Lead(Ii) from Effluents by Sorption on Peat Using Second-Order Kinetics, Separation Science and Technology 36 (2001) 241-261.

[28] Y.M. Liu, X.J. Ju, Y. Xin, W.C. Zheng, W. Wang, J. Wei, R. Xie, Z. Liu, L.Y. Chu, A novel smart microsphere with magnetic core and ion-recognizable shell for Pb^{2+} adsorption and separation, ACS applied materials & interfaces 6 (2014) 9530-9542.

[29] Y. Wang, X. Ma, Y. Li, X. Li, L. Yang, L. Ji, Y. He, Preparation of a novel chelating resin containing amidoxime–guanidine group and its recovery properties for silver ions in aqueous solution, Chemical Engineering Journal 209 (2012) 394-400.

[30] Y.G. Ko, Y.J. Chun, C.H. Kim, U.S. Choi, Removal of Cu(II) and Cr(VI) ions from aqueous solution using chelating fiber packed column: equilibrium and kinetic studies, Journal of hazardous materials 194 (2011) 92-99.

[31] A. Kandelbauer, G. Wuzella, A. Mahendran, I. Taudes, P. Widsten, Model-free kinetic analysis of melamine–formaldehyde resin cure, Chemical Engineering Journal 152 (2009) 556-565.

[32] E.K. Yetimoğlu, M. Fırlak, M.V. Kahraman, S. Deniz, Removal of Pb^{2+} and Cd^{2+} ions from aqueous solutions using guanidine modified hydrogels, Polymers for Advanced Technologies 22 (2011) 612-619.

[33] H. Aydin, Y. Bulut, C. Yerlikaya, Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents, Journal of environmental management 87 (2008) 37-45.

[34] E. Pehlivan, T. Altun, The study of various parameters affecting the ion exchange of Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} from aqueous solution on Dowex 50W synthetic resin, Journal of hazardous materials 134 (2006) 149-156.

[35] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, Journal of

the American Chemical society 40 (1918) 1361-1403.

[36] H. Freundlich, Over the adsorption in solution, J. Phys. Chem 57 (1906) e470.

[37] J. Fu, Z. Chen, M. Wang, S. Liu, J. Zhang, J. Zhang, R. Han, Q. Xu, Adsorption of methylene blue by a high-efficiency adsorbent (polydopamine microspheres): Kinetics, isotherm, thermodynamics and mechanism analysis, Chemical Engineering Journal 259 (2015) 53-61.

[38] M.X. Tan, Y.N. Sum, J.Y. Ying, Y. Zhang, A mesoporous poly-melamine-formaldehyde polymer as a solid sorbent for toxic metal removal, Energy & Environmental Science 6 (2013) 3254.

[39] X. Fu, X. Chen, J. Wang, J. Liu, Fabrication of carboxylic functionalized superparamagnetic mesoporous silica microspheres and their application for removal basic dye pollutants from water, Microporous and Mesoporous Materials 139 (2011) 8-15.

[40] C. Xiong, X. Chen, C. Yao, Study on the adsorption of Pb^{2+} from aqueous solution by D113-III resin, Desalination and Water Treatment 41 (2012) 62-71.

[41] Z. Aksu, F. Gönen, Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves, Process Biochemistry 39 (2004) 599-613.

[42] S. Araki, H. Doi, Y. Sano, S. Tanaka, Y. Miyake, Preparation and CO_2 adsorption properties of aminopropyl-functionalized mesoporous silica microspheres, Journal of colloid and interface science 339 (2009) 382-389.

[43] R.S. Vieira, M.M. Beppu, Dynamic and static adsorption and desorption of Hg(II) ions on chitosan membranes and spheres, Water research 40 (2006) 1726-1734.

[44] M. Wang, R. Qu, C. Sun, P. Yin, H. Chen, Dynamic adsorption behavior and mechanism of transition metal ions on silica gels functionalized with hydroxyl- or amino-terminated polyamines, Chemical Engineering Journal 221 (2013) 264-274.

[45] F. An, B. Gao, X. Dai, M. Wang, X. Wang, Efficient removal of heavy metal ions from aqueous solution using salicylic acid type chelate adsorbent, Journal of hazardous materials 192 (2011) 956-962.

[46] J.B. Qu, X.Z. Wan, Y.Q. Zhai, W.Q. Zhou, Z.G. Su, G.H. Ma, A novel stationary phase derivatized from hydrophilic gigaporous polystyrene-based microspheres for high-speed protein chromatography, Journal of chromatography. A 1216 (2009) 6511-6516.

(1) Monodisperse MF resin microspheres were prepared without adding any surfactant.
(2) MF resin microspheres prepared under optimal condition had a clean surface.
(3) MF resin microspheres contained abundant active amine and imine.
(4) MF resin microspheres exhibited a fast adsorption efficiency of Pb (II).