

# The Surface Modification of Magnetic Poly(methyl acrylate) Microspheres with Dendron and Application in Au(III) Adsorption

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**ABSTRACT:** An improved suspension polymerization method for preparation of the magnetic poly(methyl acrylate) microspheres (mPMA-DVB) was investigated. Through subsequent reaction with methyl acrylate (MA) and ethylenediamine (EDA), the magnetic poly(methyl acrylate) microspheres with dendron surface was obtained, and the magnetic poly(methyl acrylate) microspheres with dendron surface reacted with carbon bisulfide and sodium hydroxide to create sodium dithiocarbamate. Following, the resultant magnetic microspheres with dendron surface modification were used to adsorb Au(III) from aqueous solution. The result showed that the capacity of amino groups on the surface of the mPMA microspheres increased from 1.67 mmol/g for the magnetic polymer microspheres with  $G_0$  dendron to 4.35 mmol/g with  $G_3$

dendron, and the adsorption capacity rose from 0.1981 g/g with  $G_0$  dendron to 0.7853 g/g with  $G_3$  dendron. The effects of solution pH, the adsorption temperature, the adsorption time, and the initial concentration of Au(III) on the adsorption of Au(III) were studied, the optimum pH for Au(III) adsorption was found at pH = 1, the adsorption capacity achieved the maximum in 60 min, and the adsorption process was endothermic reaction and conformed to pseudo-second-order kinetic models. Furthermore, the adsorption process was in accordance with the Langmuir model. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** magnetic poly(methyl acrylate) microspheres; dendron surface modification; Au(III); adsorption

## INTRODUCTION

With the development of economy, the demand in many industrial activities for precious metals such as gold is constantly expanding. So it appears more important to recycle the precious metals from the secondary resources especially the industrial waste water because of the limited natural resources. Liquid–liquid extraction has been applied to remove and recover of Au(III) from the residues.<sup>1,2</sup> However, the loss of extract in the aqueous phase limits the application. One widely studied method for extracting the metals from the waste water is the usage of various adsorbents such as adsorption resins<sup>3–5</sup> and modified magnetic microspheres.<sup>6,7</sup>

Compared with the adsorption resins, the magnetic microspheres have the advantage of quick separation by external magnetic field, simple operation, high selectivity, and separation efficiency. In addition,

the magnetic microspheres surface can be modified to suit the application.<sup>8,9</sup> However, there were not enough functional groups on the surface of magnetic microspheres. To solve this problem, the magnetic microspheres can be dendron surface modified. Since the first time Buhleier et al.<sup>10</sup> tried to gradually synthesize dendrites macromolecules, the technology of dendrites macromolecule polymerization have been continuously improved.<sup>11,12</sup> Nowadays, it is widely used in many fields, such as catalysts,<sup>13</sup> capping agent,<sup>14</sup> photonic devices,<sup>15</sup> and drug-delivery systems.<sup>16–19</sup> But there are only few articles on magnetic polymer microspheres with dendron surface modification for the adsorption of precious metals as far as we know.

In this study, we modified the magnetic poly(methyl acrylate) (mPMA) microspheres with ethylenediamine (EDA) by ammonolysis. The mPMA microspheres after ammonolysis reaction were denoted as mPMA-DVB-NH<sub>2</sub>. mPMA-DVB-NH<sub>2</sub> successively reacted with methyl acrylate (MA) and EDA. And we obtained the mPMA microspheres with the first-generation ( $G_1$ ) dendron. On repeating these two steps, the mPMA microspheres with the second-generation ( $G_2$ ) dendron and the third-generation ( $G_3$ ) dendron were obtained. And mPMA-DVB-NH<sub>2</sub> was functionalized with carbon bisulfide

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and sodium hydroxide for adsorbing the Au(III) from aqueous solution. We also investigated the influence of the solution pH, the adsorption temperature, the adsorption time, and the initial concentration of Au(III) in the extraction process.

## EXPERIMENTAL

### Materials

All chemicals used were purchased from Beijing Chemical Reagents Company (Beijing, China) unless otherwise stated. MA and divinylbenzene (DVB) were distilled under reduced pressure to remove the inhibitor before use. Benzoyl peroxide (BPO) was used as inhibitor. Poly(vinyl alcohol) (PVA-1788, degree of polymerization 1700, degree of hydrolysis 88%) was used as a stabilizer. All other materials were analytical grade and used without further purification, including ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), ferrous chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), ammonium hydroxide (25% [w/w]), oleic acid, EDA, chloroacetic acid, *N,N'*-dimethyl formamide (DMF), ethanol, sodium chloroacetate, sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), sodium hydroxide (NaOH), carbon disulfide, hydrochloric acid (37% [w/w]), ethylene diamine tetraacetic acid (EDTA), and gold chloride.

### Experiments

Preparation of magnetic poly(methyl acrylate) microspheres

The mPMA microspheres were prepared as described previously.<sup>20</sup> The oleic acid-coated  $\text{Fe}_3\text{O}_4$  magnetic gel<sup>21</sup> and BPO (0.15 g) were dispersed in a mixture of MA (10 mL) and DVB (0.3 mL) to form the organic phase; PVA (3.65 g) and NaCl (3.5 g) were dissolved in  $\text{H}_2\text{O}$  (100 mL) to form the aqueous phase. The organic phase were then added into the aqueous phase and reacted for 8 h. The resulting magnetic microspheres were washed with deionized water and ethanol and the microspheres were stored in ethanol before use.

Surface dendron modification of the magnetic poly(methyl acrylate) microspheres

mPMA-DVB (2 g) was washed with DMF two times and put in a solution of 100 mL DMF and 100 mL EDA. The mixture was agitated gently at 80°C for 8 h, after being cooled to room temperature, the magnetic polymer microspheres were separated by magnetic decantation and washed with water and ethanol to remove the residual DMF. After modification, ester groups on the microspheres were con-

verted into amino groups. The mPMA microspheres were denoted as mPMA-DVB-NH<sub>2</sub>-G<sub>0</sub>.

Divergent synthesis was adopted to modify the mPMA-DVB-NH<sub>2</sub>; mPMA-DVB-NH<sub>2</sub> (2 g) was mixed with 100 mL DMF and 100 mL MA. The mixture was agitated gently at 80°C for 8 h. After being cooled to room temperature, the magnetic polymer microspheres were separated by magnetic decantation and washed with water and ethanol to remove the residual MA and DMF.

The mPMA-DVB-NH<sub>2</sub> reacted with EDA as described above, so the first-generation (G<sub>1</sub>) dendron was obtained, and the process of synthesis of G<sub>2</sub> and G<sub>3</sub> as described above.

A 2 g sample of mPMA-DVB-NH<sub>2</sub>-G<sub>1</sub> was added into the mixture of 16 g carbon bisulfide and 30 mL 6% NaOH, with agitation at 500 rpm for 2 h at room temperature, the temperature was increased evenly to 45°C for 4 h. After reaction, the magnetic polymer microspheres which were denoted as mPMA-DVB-NH<sub>2</sub>-G<sub>1</sub>-CS were separated by magnetic decantation and washed with water to remove the residues.

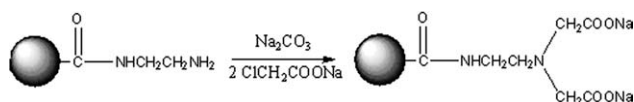
The application of magnetic poly(methyl acrylate) microspheres for Au (III) adsorption

A certain sample of mPMA-DVB-NH<sub>2</sub>-G<sub>1</sub>-CS was added into the mixture of hydrochloric acid and Au(III), with agitation for 1 h at different temperatures. The mPMA-DVB-NH<sub>2</sub>-G<sub>1</sub>-CS was separated by external magnetic field. The concentration of the residual Au(III) was characterized by atomic absorption spectrophotometric apparatus (AAS, AA-6800, Shimadzu, Tokyo, Japan). According to the change of the concentration of Au(III), calculated the adsorption percentage of the magnetic polymer microspheres.

The recovery of Au(III) can be carried out by the steps as follows: added a certain sample of the magnetic polymer microspheres which were chelated with Au(III) into the 10% (w/w) thiourea solution, the mixture was adjusted to pH = 0 with HCl. After agitation for 1 h at room temperature, the magnetic polymer microspheres were separated by the external magnetic field. The concentration of Au(III) in the solution was characterized by AAS.

### Characterization

The morphology and the size of mPMA microspheres were determined by biological microscope photograph (BMP, BK 300, OPTEC). The magnetization curves of the dried mPMA microspheres were recorded with a vibrating sample magnetometer (VSM) (Model-155, Inc). Fourier transform infrared spectroscopy (FTIR) spectra of both the unmodified and modified mPMA microspheres were obtained



**Scheme 1** The microspheres reacted with sodium chloroacetate.

with a FTIR spectrophotometer (FT-IR, 670, Thermo Nicolet Corporation).

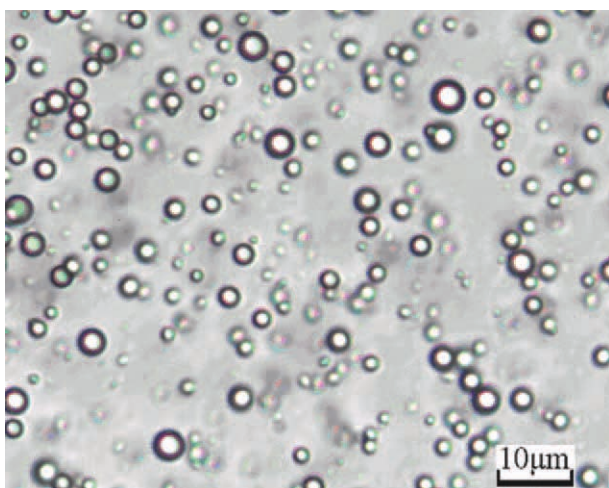
The capacity of amino groups on the surface of the magnetic polymer microspheres was obtained by indirectly determining the concentration of  $\text{Cu}^{2+}$ . Three grams of sodium chloroacetate and 2 g  $\text{Na}_2\text{CO}_3$  were dissolved in 100 mL water, the mixture was then transferred into 250-mL neck flask containing 2 g modified microspheres. With agitation at 600 rpm, the temperature was maintained at  $70^\circ\text{C}$  for 8 h. After the mixture was cooled to room temperature, the mixture was washed with water to remove the residues. The reaction is detailed in Scheme 1.<sup>20</sup>

Then the microspheres were put into the  $\text{CuSO}_4$  (0.1 mol/L), the mixture was agitated at 200 rpm at room temperature for 2 h and washed with water to remove the residual  $\text{Cu}^{2+}$ . After the microspheres in the oven were dried for 2h, the microspheres were put in the 20 mL 0.01mol/L EDTA for 10 min. The concentration of  $\text{Cu}^{2+}$  in the EDTA solution was characterized by AAS (AA-6800, Shimadzu).

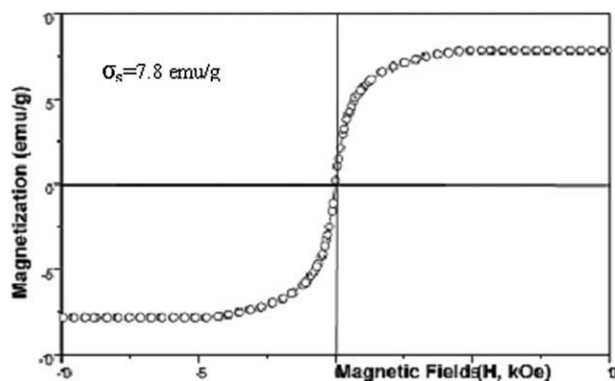
## RESULTS AND DISCUSSION

### Preparation and characterization of the magnetic poly(methyl acrylate) microspheres

The mPMA-DVB was prepared by an improved suspension polymerization. Figure 1 shows the BMP photographs of mPMA-DVB. The microspheres were



**Figure 1** NA micrograph of mPMA-DVB. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 2** Magnetization curves of mPMA-DVB.

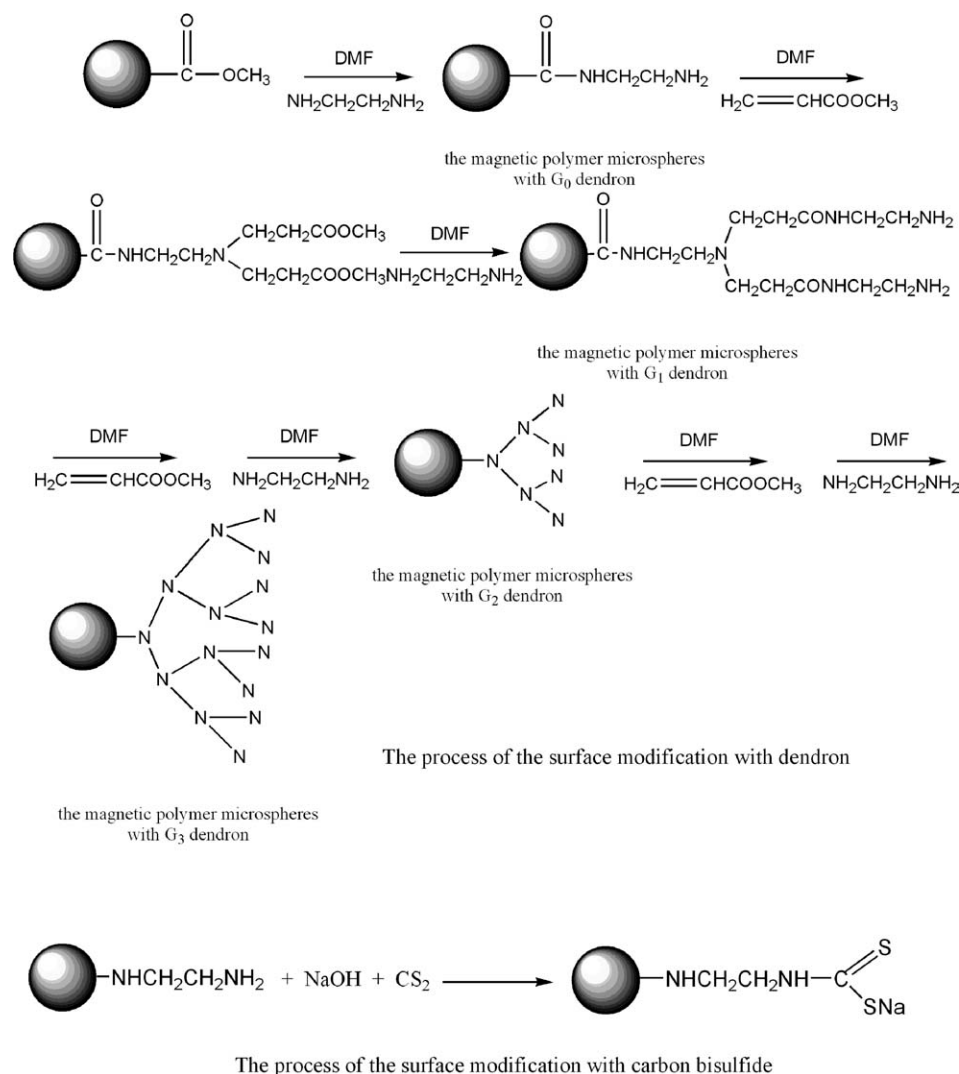
spherical and the surface was smooth. The average number diameter of magnetic mPMA-DVB microspheres was  $3.0\ \mu\text{m}$ .

The magnetic properties of mPMA-DVB were recorded by VSM at room temperature. Figure 2 shows their magnetization curves. There was no hysteresis loop observed, thus indicating that the magnetic microspheres were superparamagnetic, and this would result in the easy dispersion of magnetic microspheres. The saturation magnetization of the magnetic microspheres was 7.8 emu/g. With such saturation magnetization, mPMA-DVB could be easily and quickly separated from a suspension. This is favorable for the magnetic separation of solutions.

In order to investigate the stability of mPMA-DVB under acidic condition, the concentration of Fe(II) and Fe(III) in the solution is characterized by AAS apparatus. The results showed that there was almost no dissolution of  $\text{Fe}_3\text{O}_4$  in the solution when  $\text{pH} > 1$ . At  $\text{pH} = 1$ , the leaching extent (w/w) of Fe from the microspheres was 0.9%, and it increased to 1.5% at  $\text{pH} = 0$ . It indicated that  $\text{Fe}_3\text{O}_4$  were coated incompletely.

### Surface dendron modification of the magnetic poly(methyl acrylate) microspheres

The amino groups on the surface of mPMA-DVB- $\text{NH}_2$  were produced with EDA as shown (Scheme 2).<sup>22,23</sup> To increase the number of amino groups on the surface of magnetic microspheres, the magnetic polymer microspheres were reacted with MA and EDA repeatedly. The process (Scheme 2)<sup>22,23</sup> involves two consecutive chain-forming reactions, the exhaustive Michael additions reaction and the exhaustive amidation reaction. On repeating these two steps alternatively the higher generation of dendron can be obtained. To increase the capacity of recovery, the magnetic polymer microspheres were reacted with carbon bisulfide and NaOH, as shown in Scheme 2.<sup>22,23</sup> The structure of  $\text{C}=\text{S}$  and  $\text{C}-\text{S}$  are ready for chelating the Au(III), and can be easy to be recovered by the thiourea.



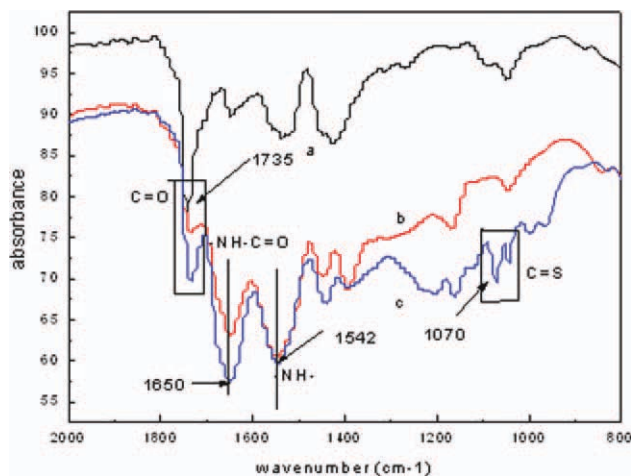
**Scheme 2** The surface modification process of the magnetic polymer microspheres.

The FTIR spectra were recorded in the absorbance mode on a Fourier transform infrared spectrophotometer. Figure 3 shows the spectrum of microspheres. The stretching vibration of C=O downshifts to  $1650\text{ cm}^{-1}$ ,<sup>24</sup> but there still existed a peak at  $1735\text{ cm}^{-1}$ , suggesting that the ammonolysis was not complete. The presence of N–H in magnetic microspheres was confirmed from a distinct characteristic peak at  $1542\text{ cm}^{-1}$ ,<sup>24</sup> peak at  $1070$ , and  $1040\text{ cm}^{-1}$  suggested the existence of C=S.<sup>25</sup>

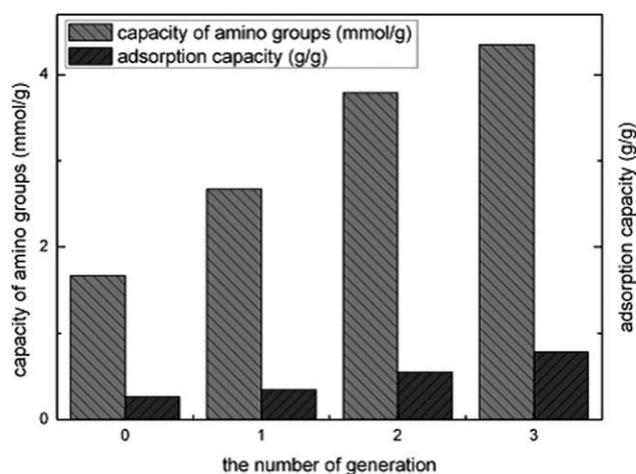
### The adsorption of Au (III) by use of magnetic poly(methyl acrylate) microspheres

The effect of the magnetic polymer microspheres with different generation of dendron

Constant experimental conditions were 10 mg microspheres, 0.1530 g/L Au(III), pH = 1, the extraction time is 60 min, and 20°C temperature.



**Figure 3** FTIR spectra of (a) the mPMA-DVB microspheres, (b) the mPMA-DVB-NH<sub>2</sub> microspheres, (3) the magnetic PMA-DVB-NH<sub>2</sub>-CS microspheres. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 4** The relationship of the number of grafted generation with capacity of amino groups on the surface of magnetic microspheres and adsorption capacity, respectively.

The capacity of amino groups were obtained by indirectly determining the capacity of Cu(II). Although the transformation of surface  $-\text{NH}_2$  to  $-\text{COONa}$  and  $-\text{COONa}$  to  $-(\text{COO})_2\text{Cu}^{2+}$  are not complete, it almost approach the complete reaction in this experimental conditions. So we consider the capacity of amino groups equal to the capacity of Cu(II). Figure 4 shows the capacity of amino groups for  $G_0$ ,  $G_1$ ,  $G_2$ , and  $G_3$ , and the capacity was greatly increased from  $1.67 \pm 0.027$  mmol/g for the magnetic polymer microspheres with  $G_0$  dendron to  $4.35 \pm 0.034$  mmol/g for the magnetic polymer microspheres with  $G_3$  dendron after dendron surface modification. And the adsorption capacity per mass microspheres (Fig. 4) rose from  $0.1981 \pm 0.002$  g/g for the magnetic polymer microspheres with  $G_0$  dendron to  $0.7853 \pm 0.0035$  g/g for the magnetic polymer microspheres with  $G_3$  dendron.

The yield was calculated from the relation [eq. (1)],  $C_N$   $C_{N-1}$  represent the capacity of amino groups on the surface of the magnetic polymer microspheres with  $G_N$  dendron (mmol/g). It indicated that the yield decreased with the increasing of the dendron generation (Table I). It is most likely because when EDA modified the microspheres, EDA molecules reacted with the second ester, and it produced the bridge-type structure, this structure prevented the amino groups reacting with MA. In addition, the activity of the tertiary amines are much weaker than the primary amines, in this experimental conditions,

**TABLE I**  
The Yield and Extraction Percentage of the Magnetic Poly (methyl acrylate) Microspheres with Different Generation of Dendrons

generation of dendron	G0	G1	G2	G3
yield %	-	60	41.9	14.8
adsorption percentage %	60.2	66.2	73.4	91

the tertiary amines barely react with EDA. This resulted in the decrease of the grafted ratio.

$$G_N = \frac{C_N - C_{N-1}}{C_{N-1}} \quad (1)$$

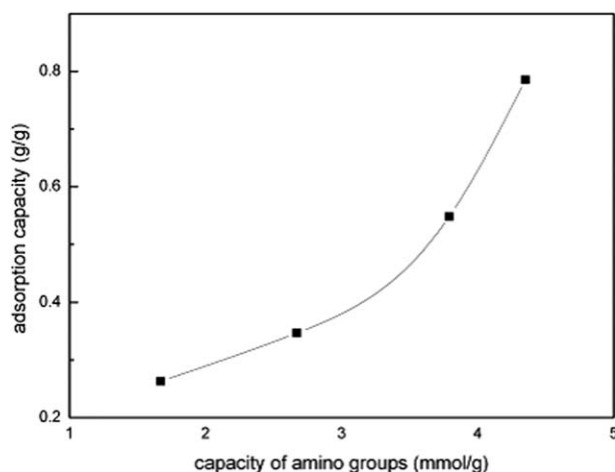
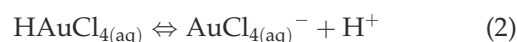
However, the adsorption percentage of Au(III) increases with the rise of generation of dendron. Figure 5 shows the relationship between the capacity of amino groups and adsorption capacity. Adsorption capacity gradually increases as the capacity of amino groups increases, and also the adsorption percentage gradually increases. In fact, the adsorption percentage varied from 60.2% to 91% after being calculated. Because the space on the surface of the magnetic microspheres was enough for the Au(III) to access the amino groups, and the process of adsorption is chemical adsorption, the more amino groups on the surface, the more complete the adsorption process.

In addition, the magnetic polymer microspheres were put into the mixture of 10% (w/w) thiourea and 1 mol/L HCl, the back extraction is 95.3%.

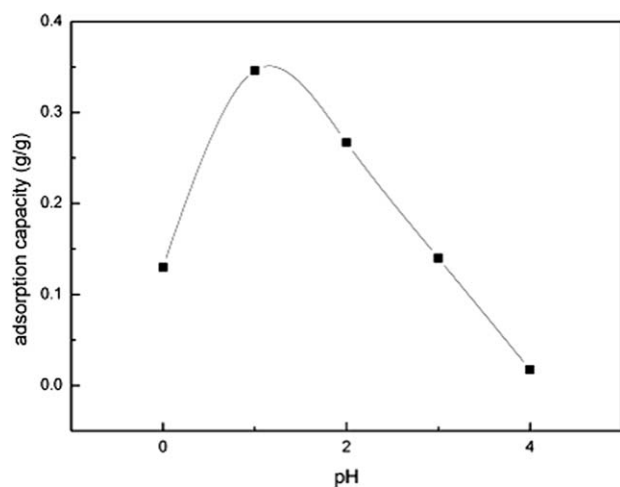
The effect of the aqueous pH on the Au(III) adsorption

Constant experimental conditions were 10 mg mPMA-DVB-NH<sub>2</sub>-G<sub>1</sub>-CS, 95.64 mg/L Au(III), the adsorption time is 60 min and 20°C temperature, pH was varied from 0 to 4.

The results (Fig. 6) show the highest adsorption capabilities of the microspheres at pH =1. In the aqueous solution of pH < 1, Au(III) most likely exists as chloroauric acid (HAuCl<sub>4</sub>) species, which is less dissociated at lower pH as follows:

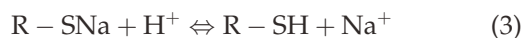


**Figure 5** The relationship between the capacity of amino groups and adsorption capacity.



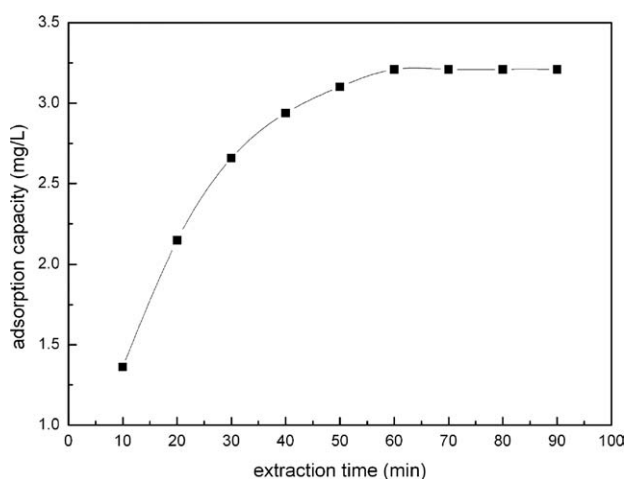
**Figure 6** Effect of the solution pH on adsorption capacity.

Thus, the equilibrium [eq. (2)] moves to the left at the low pH and the quantity of  $\text{AuCl}_{4(\text{aq})}^-$  ion available to form complex ion associate with the magnetic microspheres decreased. This results in the decrease of the adsorption capacity. On the other hand, in aqueous solution of  $\text{pH} > 1$ , the Au(III) adsorption decreased as the HCl concentration decreased. It most likely the equilibrium [eq. (3)] moves to the left when the low concentration of  $\text{H}^+$ , this result makes the equilibrium [eq. (4)]<sup>26</sup> moves to the left.

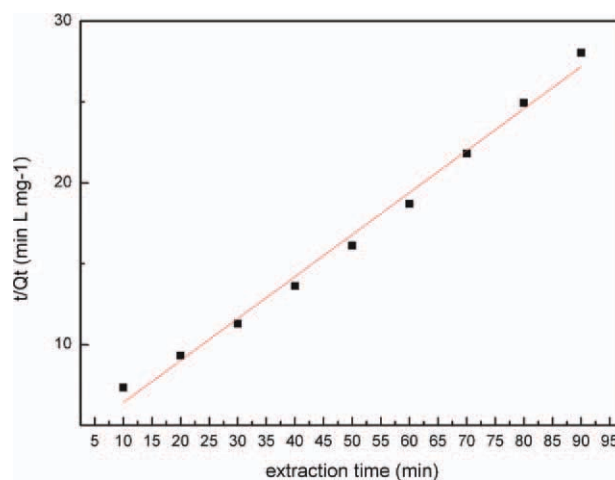


The effect of time on the Au(III) adsorption

Constant experimental conditions were 10 mg mPMA-DVB-NH<sub>2</sub>-G<sub>1</sub>-CS, 95.64 mg/L Au(III), the temperature of adsorption is 20°C, and pH = 1, the adsorption time varied from 10 min to 90 min.



**Figure 7** The effect of time on the adsorption capacity.

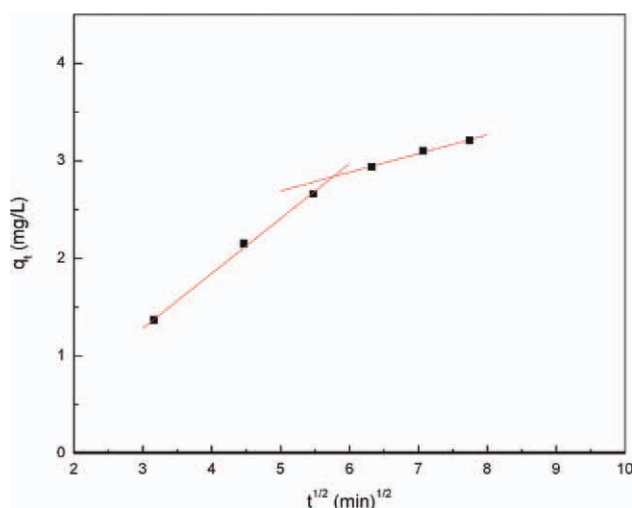


**Figure 8** The adsorption kinetics of microspheres toward Au(III). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

As seen from Figure 7, the adsorption occurred quickly compared with others<sup>27</sup> and could be finished within 60 min. According to pseudo-second-order kinetic models, there exists the following relation between  $t$  and  $Q_t$  [eq. (5)], the variables  $Q_t$  and  $Q_{\text{ex}}$  represent the adsorption capacity (mg/L) at adsorption time  $t$  and at equilibrium, respectively. The linear plot (Fig. 8) of  $t/Q_t$  versus time can be obtained based on the data. So the rate constant  $k$  ( $8.57 \times 10^{-4}$  L/(mg min)) of the pseudo-second-order kinetics equation can be obtained from the intercept. And correlation factor  $R^2 = 0.991$ , it indicates that the adsorption capacities at equilibrium calculated from the kinetic equation are in agreement with the experimental data. In addition, the pseudo-second-order kinetic model basically considers external film diffusion, intra-particle diffusion, and chemical reaction for adsorption process.<sup>28</sup> The external film diffusion is eliminated by stirring. So, the adsorption rate may be controlled by intra-particle diffusion or chemical reaction. And to decide which kind of diffusion is the rate-limiting step, an internal diffusion model based on Fick's second law is used, the equation is as follows:

$$Q_t = k_{\text{id}} t^{1/2} + C$$

where  $Q_t$  is the adsorption capacity of the magnetic polymer microspheres (mg/L),  $k_{\text{id}}$  is the intra-particle diffusion rate constant (mg/L min<sup>1/2</sup>) and  $C$  is a constant. According to Figure 9, there are two portions. The first portion is due to the external diffusion and the surface adsorption stage, then the final equilibrium stage. In this case, the plots in Figure 9 suggest that there are two steps in the process of adsorption: the beginning (1–30 min) and the plateau (30–60 min). The initial linear portion is the



**Figure 9** The relationship between  $Q_t$  and  $t^{1/2}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

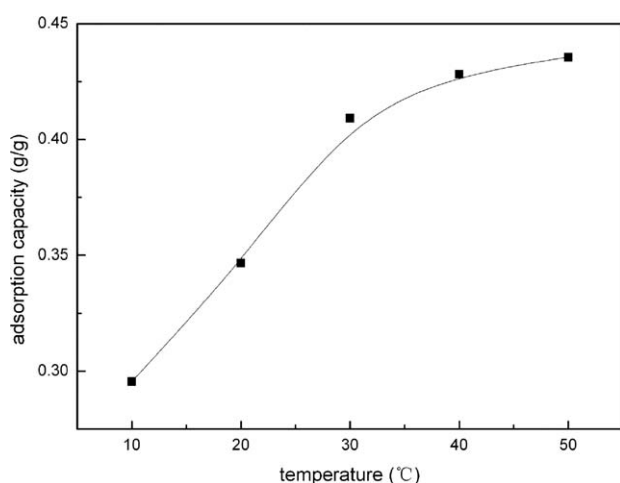
gradual adsorption stage, in this stage intra-particle diffusion is rate-controlled. The following linear portion is the final equilibrium stage, where the intra-particle diffusion slows down.

$$\frac{t}{Q_t} = \frac{1}{kQ_{ex}^2} + \frac{t}{Q_{ex}} \quad (5)$$

The effect of temperature on the Au(III) adsorption

30.4 mg mPMA-DVB-NH<sub>2</sub>-G<sub>1</sub>-CS were divided into four parts accurately, then every part was mixed with Au(III) solution (95.64 mg/L) then the solution was adjusted to pH = 1 with HCl, each extracted Au(III) under constant temperature for an hour at 20°C, 30°C, and 40°C, respectively.

Figure 10 shows the relationship between the adsorption temperature and the adsorption capacity. It suggested that the adsorption capacity increased



**Figure 10** The relationship between the adsorption temperature and the adsorption capacity.

**TABLE II**

**Influence of Temperature on Distribution Coefficient**

T/K	283	293	303	313	323
1/T( $\times 10^{-3}$ )	3.532	3.413	3.300	3.195	3.095
D	0.3076	0.3805	0.4467	0.5098	0.5886

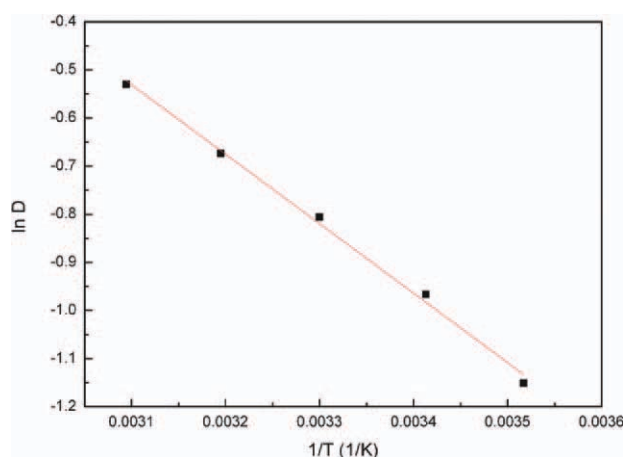
with the raised temperature. From the point of thermodynamic, adsorption of Au(III) can be regarded as a transfer process of Au(III) from the aqueous phase to the solid phase. To calculate the thermodynamic characteristics, equilibrium constants were determined at different temperatures. Measuring the mass concentration of Au(III) by atomic adsorption spectrophotometer when the adsorption at its equilibrium. The distribution coefficient  $D$  (also  $K_{ex}(T)$  at this condition) [eq. (6)] is shown in Table II. The variables  $C_{ex}$  and  $Q_{ex}$  represent the residual metal capacity (mg/L) in the solution after adsorption and the adsorption capacity (mg/L) of the magnetic polymer microspheres at equilibrium, and  $K_{ex}(T)$  is the equilibrium constant at temperature  $T$ .

$$K_{ex}(T) = D = \frac{Q_{ex}}{C_{ex}} \quad (6)$$

According to Van't Hoff equation [eq. (7)], the enthalpy change  $\Delta H^0$  and the entropy change  $\Delta S^0$  for adsorption can be estimated by the intercept and the slope of the liner plot of  $\ln K_{ex}(T)$  versus  $1/T$  (Fig. 11). After being calculated,  $\Delta H^0 = 11.99$  kJ/mol and  $\Delta S^0 = 32.78$  J/(mol K).

$$\ln K_{ex}(T) = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (7)$$

The positive value of  $\Delta H^0$  shows that the adsorption is endothermic, raising the temperature leads to a



**Figure 11** Effect of adsorption temperature on distribution coefficient. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

higher adsorption of the magnetic polymer microspheres at equilibrium. The positive value of  $\Delta S^0$  means a increase in the order of the system, it is mainly due to the release of the molecule of water when the adsorbate react with the functional groups on the surface of the magnetic polymer microspheres.

The effect of the initial concentration on the Au(III) adsorption

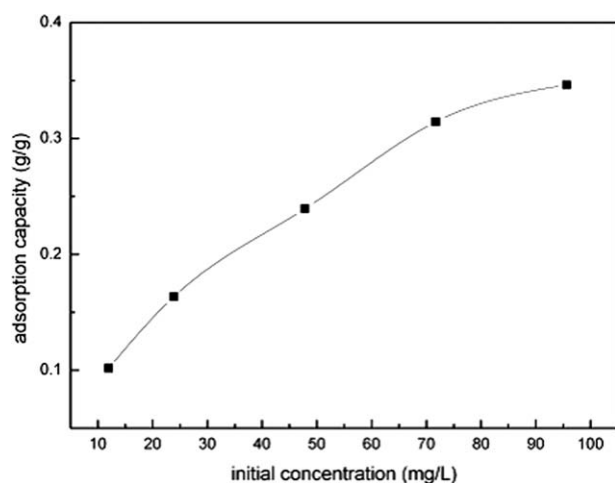
The effect of the initial concentration of Au(III) on the adsorption capacity was investigated. The result is shown in Figure 12. The adsorption capacity increased with the initial concentration.

The adsorption equilibrium of metal ions between aqueous solution and the magnetic microspheres can be described by an adsorption isotherm. Langmuir [eq. (8)] and Freundlich model [eq. (9)] were adopted. As we know, the Langmuir equation is applicable to homogeneous adsorption, while the Freundlich equation is employed to describe heterogeneous systems.  $Q_{ex}$  and  $C_{ex}$  are the adsorption capacity (mg/L) and the residual metal concentration (mg/L) in solution at equilibrium.  $b$  and  $Q_0$  are the Langmuir constant (L/mg) and maximum adsorption capacity (mg/L),  $K_f$  and  $n$  are Freundlich constants.

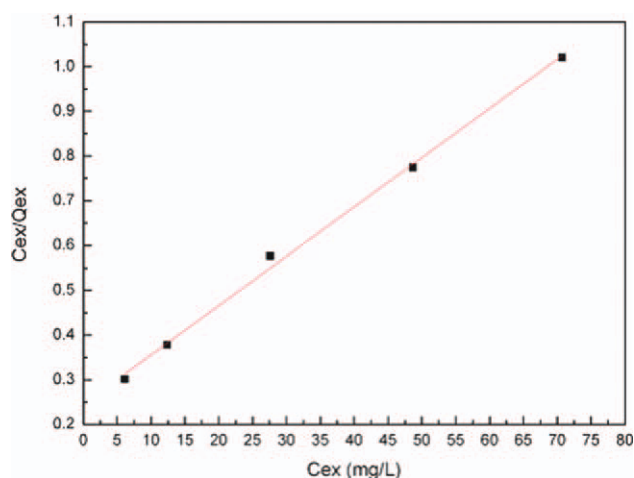
$$\frac{C_{ex}}{Q_{ex}} = \frac{C_{ex}}{Q_0} + \frac{1}{bQ_0} \quad (8)$$

$$\ln Q_{ex} = \ln K_f + \frac{1}{n} \ln C_{ex} \quad (9)$$

Plotting  $\frac{C_{ex}}{Q_{ex}}$  versus  $C_{ex}$  and  $\ln Q_{ex}$  versus  $\ln C_{ex}$ , respectively, two lines were obtained. And the experimental data fit to the Langmuir model (Fig. 13) ( $R^2 = 0.996$ ) better than the Freundlich model ( $R^2 = 0.984$ ). The Langmuir constant ( $b$ ) calculated from the line is 0.0448 L/mg.



**Figure 12** The relationship between the initial concentration of Au(III) and adsorption capacity.



**Figure 13** Langmuir plot for the adsorption toward Au(III). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The degree of suitability of particles toward Au(III) was estimated from the values of the separation factor constant ( $R_L$ ), it is also the essential feature of Langmuir adsorption isotherm.  $R_L > 1.0$  unsuitable;  $R_L = 1$  linear;  $0 < R_L < 1$  suitable;  $R_L = 0$  irreversible.<sup>29</sup> The value of  $R_L$  could be calculated from the relation:

$$R_L = \frac{1}{1 + bC_0} \quad (10)$$

$C_0$  is the initial concentration (mg/L) of Au(III). The values of  $R_L$  lie between 0.189 and 0.651 indicating the suitability of the magnetic polymer microspheres toward Au(III). For Freundlich isotherm,  $n$  is equal to 1.994. The situation  $n > 1$  is most common, and when the values of  $n$  is in the range of 2–10, it means good adsorption, otherwise it represents bad adsorption.<sup>30</sup>

## CONCLUSION

The following conclusions have been drawn from this investigation:

1. An improved suspension polymerization method was adopted for the preparation of mPMA-DVB. The magnetic polymer microspheres were spherical and the surface was smooth, the average number diameter of the microspheres is 3.0  $\mu\text{m}$ .
2. The capacity of amino groups on the surface of the magnetic polymer microspheres were greatly increased after dendron surface modification. It increased from 1.67 mmol/g for mPMA-DVB with  $G_0$  dendron to 4.35 mmol/g for mPMA-DVB with  $G_3$  dendron. The adsorption capacity also rose from 0.1981 g/g with  $G_0$  dendron to 0.7853 g/g with  $G_3$  dendron.



3. The magnetic polymer microspheres shows good adsorption activity on Au(III), the result showed that the optimum pH for Au(III) adsorption was found at pH = 1, the adsorption capacity achieved the maximum in 60 min, the adsorption process for the mPMA microspheres was endothermic reaction and conformed to pseudo-second-order kinetic models. Furthermore, the adsorption process was in accordance with the Langmuir model.

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