

## Tetraethylenepentamine-modified cellulose-graft-poly(methyl acrylate) applicable for Pb(II) adsorption from aqueous solution

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Tetraethylenepentamine-modified cellulose-graft-poly(methyl acrylate) (Cell-g-PMA-TEPA), a polyamino-functionalized adsorbent for Pb(II), has been prepared via graft polymerization of methyl acrylate (MA) from surface of microcrystalline cellulose and subsequent amidation with tetraethylenepentamine (TEPA). Influence of initial pH and contact time on adsorption has also been investigated. The adsorption kinetic could be best represented by pseudo-second-order model, while equilibrium data fits well with Langmuir isotherm model, from which maximum adsorption capacity could be derived as 444.4 mg g<sup>-1</sup>. Further consecutive experiments indicate less than 10% loss in equilibrium adsorption capacity after five adsorption-desorption cycles.

**Keywords:** Adsorption, Cellulose, Graft polymerization, Pb(II), Polyamine, Poly(methyl acrylate)

Heavy metal pollution has become a great concern in environmental protection since heavy metals might reduce production and quality of crops and aquatic products and are generally considered to be a threat toward humans and ecosystems<sup>1-3</sup>. Specifically, lead has been recognized as one of the most hazardous heavy metals which may cause severe damage to vital organs of human beings such as kidney, liver, blood composition, nervous system, reproductive system as well as mental retardation in children<sup>4-7</sup>. For this reason, it is necessary to remove heavy metal ions from household and industrial waste water.

In recent years, several methods have been developed for removal of heavy metals ions from aqueous solution. Compared with conventional technique such as chemical precipitation, flocculation, membrane separation, ion exchange, evaporation and electrolysis<sup>8-12</sup>, adsorption procedure has been proven to be more effective, efficient and economical in removing heavy metal ions and dyes from waste streams and drinking water<sup>13-15</sup>.

Due to chemically active hydroxyl groups in its structure, cellulose is considered an excellent candidate for preparation of various chelate materials<sup>16,17</sup>. For instance, kapok fiber has been chemically modified with diethylenetriaminepentaacetic acid for fast

adsorption of heavy metal ions<sup>18</sup>. Furthermore, grafting copolymerization of reactive monomers from cellulose has become an attractive and versatile technique for imparting a variety of functional groups to cellulose in developing efficient adsorbents for heavy metal ions<sup>19,20</sup>. To the best of our knowledge, glycidyl methacrylate (GMA) and acrylonitrile (AN) are more commonly used as monomers for graft polymerization from cellulose surface and then functionalized with polyamines, hydroxylamine, imidazole and hydrazine to improve adsorption behaviour<sup>21-24</sup>. There have also been certain investigation about modification of cellulose-graft-poly(methyl acrylate) (Cell-g-PMA) with hydroxylamine and hydrazine, rendering 75 mg g<sup>-1</sup> and greater maximum adsorption capacity for Cu(II) and Ni(II) adsorption<sup>16,25-27</sup>.

Although tetraethylenepentamine (TEPA), a typical water-soluble polyamine bearing five amino groups in molecule, has exhibited strong chelating ability for parts of heavy metal ions<sup>21</sup>, TEPA-functionalized cellulose for removal of Pb(II) has been less investigated. In this study, a polyamino-modified cellulose-based adsorbent has been prepared by ceric salt-initiated grafting polymerization of methyl acrylate (MA) from microcrystalline cellulose and

subsequent amidation with TEPA. The adsorption property of thus amidated Cell-g-PMA (Cell-g-PMA-TEPA) for Pb(II) has also been examined in detail.

## Experimental Section

### Materials

Reagent-grade microcrystalline cellulose was dried in vacuum at 50°C to constant weight prior to use. Tetraethylenepentamine (TEPA, 95%) and lead nitrate were obtained from Aladdin Reagent (China). The monomer, methyl acrylate (MA, 99.5%) was purchased from J&K Scientific Ltd. Nitric acid and ceric ammonium nitrate (CAN, 99%) were provided by Sinopharm Chemical Reagent Co., Ltd. Sodium hydroxide, hydrochloric acid, ethanol and anhydrous acetone were purchased from local chemical suppliers. All the solvents and reagents were used as received except that MA was distilled under reduced pressure before graft polymerization.

### Preparation of tetraethylenepentamine-modified cellulose-graft-poly(methyl acrylate)

Tetraethylenepentamine-modified cellulose-graft-poly(methyl acrylate) (Cell-g-PMA-TEPA) was prepared by a two-step procedure. In the first step, dried microcrystalline cellulose (0.5 g) and 20 mL of 0.1 mol L<sup>-1</sup> nitric acid were mixed in a 50 mL three necked round-bottomed flask, followed by bubbling with nitrogen over 20 min. CAN (0.06 g, 0.11 mmol) was added and homogenized with magnetic stirrer, when the temperature of mixture was maintained at 30°C for 20 min. Then, monomer MA (1.9 g, 22 mmol) was added to above suspension with constant stirring and allowed to react at 35°C for another 1.5 h. Crude product was collected after filtration and alternate washing with deionized water and ethanol to remove unreacted monomer. Subsequently, homopolymer was removed by Soxhlet extraction with acetone and residual cellulose-g-poly(methyl acrylate) (Cell-g-PMA) was vacuum dried at 40°C until constant weight with white solid left. Graft percentage  $G_p$  (%) was calculated by percentage increase in mass as follows:

$$G_p = 100(w_2 - w_1)/w_1 \quad \dots (1)$$

where  $w_2$  (g) and  $w_1$  (g) are weights of grafted and initial cellulose, respectively.

In the second step, Cell-g-PMA (1 g, 300% of  $G_p$ ) was dispersed in 40 mL anhydrous acetone solution and was stirred for 0.5 h. TEPA (34g, 0.17mol) was

then added and the mixture was further stirred at 100°C for 10 h. The suspension was separated via filtration before cooled to room temperature. The yellow solid residue was alternately washed with deionized water and ethanol, and finally dried in vacuum at 60°C to constant weight, yielding TEPA-modified Cell-g-PMA (Cell-g-PMA-TEPA).

### Characterization

Fourier transform infrared spectroscopy (FT-IR) of cellulose, Cell-g-PMA and Cell-g-PMA-TEPA were recorded using a Fourier-transform infrared spectrometer (FT-IR, Vertex70, Bruker Co., Germany). Solid-state <sup>13</sup>C NMR was obtained on a Bruker NMR spectrometer (NMR, Avance 400M, Bruker Co., Germany) at 400 MHz. Morphologies of samples were performed using a scanning electron microscope (SEM) (Nova NanoSEM NPEP281) operating at 5 kV. Concentration of Pb(II) in solution was determined by a flame atomic absorption spectrophotometer (AAS, novAA300/400FL, Analytic Jena AG Co., Germany).

### Batch adsorption experiments

For evaluating adsorption property of adsorbent, batch experiments were carried out in shaking table at 120 rpm and 28 ± 1°C using 100 mL Erlenmeyer flasks. Adsorption capacity  $Q_e$  (mg g<sup>-1</sup>) and removal efficiency  $R_e$  (%) at equilibrium were calculated using the following equations:

$$Q_e = V(C_0 - C_e)/w \quad \dots (2)$$

$$R_e = 100(C_0 - C_e)/C_0 \quad \dots (3)$$

where  $C_0$  and  $C_e$  (mg L<sup>-1</sup>) are concentrations of Pb(II) at initial and equilibrium stages,  $V$  (mL) is volume of Pb(II) solution and  $w$  (g) is the weight of adsorbent used in adsorption experiments. To study effect of initial pH on adsorption of Pb(II), pH value of about 320 mg L<sup>-1</sup> Pb(II) solution was calibrated with 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> and NaOH solutions with adsorption time being 12 h. Kinetic experiments of Pb(II) adsorption were performed at pH 5.0 to examine adsorption process at Pb(II) concentration of 650 mg L<sup>-1</sup>. For adsorption isotherms at pH value of 5.0, Pb(II) concentrations were set from 352 to 712 mg L<sup>-1</sup> with adsorption time being 12 h.

Dynamic adsorption and desorption have also been conducted to verify reusability of adsorbent with a

glass chromatographic column (inner diameter: 10 mm) filled with 0.2 g of Cell-g-PMA-TEPA. Regeneration efficiency of adsorbent for Pb(II) was evaluated at pH value of 5.0 with initial concentration of Pb(NO<sub>3</sub>)<sub>2</sub> being 3 mmol L<sup>-1</sup>.

## Results and Discussion

### Characterization of adsorbent

Among various chemical initiation methods applied in grafting polymerization of vinyl monomers from cellulose, formation of free radicals on cellulose molecules by direct oxidation with Ce (IV) ions has gained considerable importance due to high grafting efficiency<sup>19</sup>. In present study, graft percentage of Cell-g-PMA, expressed as G<sub>p</sub> in Equation (1), as high as 300% could be easily achieved. Cell-g-PMA-TEPA was successfully prepared by amidation of Cell-g-PMA with TEPA which acts as both a solvent and a reactant. The results of elemental analysis were summarized in Table 1. It was found that there was little nitrogen (0.03%) in cellulose and Cell-g-PMA, while an obvious increase in relative nitrogen

composition (19.20%) was observed after modification with TEPA, which confirmed successful preparation of Cell-g-PMA-TEPA through amidation of Cell-g-PMA.

The FT-IR spectra of cellulose, Cell-g-PMA and Cell-g-PMA-TEPA are shown in Fig. 1.

Compared with spectrum of cellulose in Fig. 1a, a new absorption peak at 1735 cm<sup>-1</sup> corresponding to carbonyl group in acrylate unit appeared and absorption peak at 1448 cm<sup>-1</sup> capable of being assigned to C-H vibration was obviously strengthened in Fig. 1b, indicating that MA had been successfully graft polymerized from cellulose. After amidation reaction, it was observed in Fig. 1c that absorption at 1735 cm<sup>-1</sup> was weakened, and a new adsorption band appeared at 1663 cm<sup>-1</sup> for carbonyl group in amide (secondary amide I band). In addition, two new bands appeared at 1566 cm<sup>-1</sup> and 1059 cm<sup>-1</sup> in Fig. 1c, which could be assigned to bending vibration of N-H (secondary amide II band) and stretching vibration of C-N in TEPA<sup>28,29</sup>, respectively, revealing that Cell-g-PMA has been successfully modified with TEPA through amidation of ester groups in acrylate units.

Solid-state <sup>13</sup>C-NMR spectroscopy was used to characterize cellulose, Cell-g-PMA, and Cell-g-PMA-TEPA in Fig. 2, respectively. In Fig. 2a, all signals, i.e. those at 105.3 ppm (C<sub>1</sub>), 88.7 ppm (C<sub>4</sub>), 72.6 ppm (C<sub>2</sub>, C<sub>3</sub> and C<sub>5</sub>), and 65.0 ppm (C<sub>6</sub>), were characteristic peaks of cellulose<sup>30</sup>. The spectrum of Fig. 2b exhibited two extra peaks at 52.0 ppm and

Material	Carbon Content (wt%)	Hydrogen content (wt%)	Nitrogen content (wt%)	C <sub>TEPA</sub> (mmol g <sup>-1</sup> )
Cellulose	42.78	6.31	0.03	-
Cell-g-PMA	52.07	7.045	0.03	-
Cell-g-PMA-TEPA	52.61	9.32	19.20	2.74

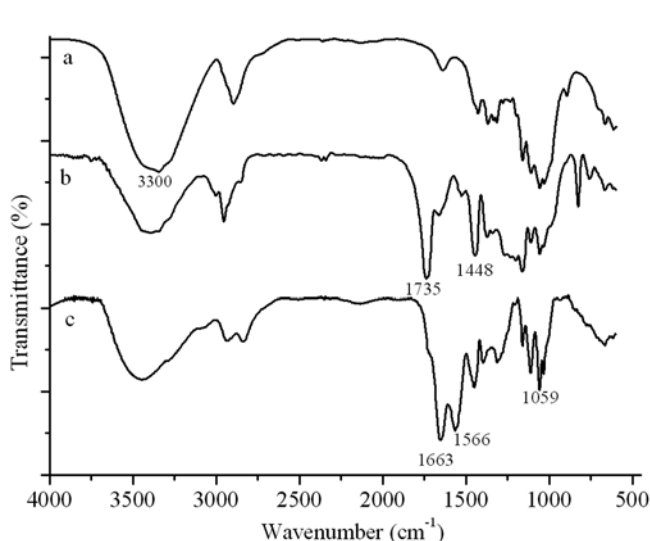


Fig. 1 — FT-IR spectra of cellulose (a); Cell-g-PMA (b) and Cell-g-PMA-TEPA (c)

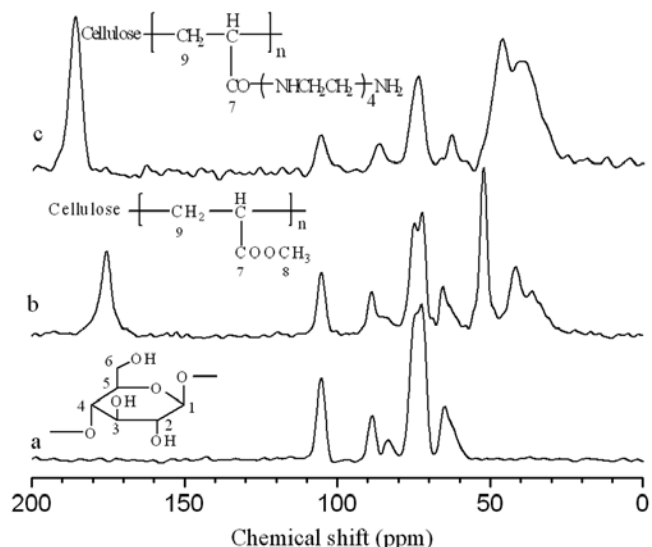


Fig. 2 — Solid-state <sup>13</sup>C NMR spectra of cellulose (a); Cell-g-PMA (b) and Cell-g-PMA-TEPA (c)

175.4 ppm corresponding to C<sub>8</sub> and C<sub>7</sub> in grafted chains of PMA. Comparison of Fig. 2b and Fig. 2c showed that one typical chemical shift for C<sub>8</sub> was weakened after amidation reaction, indicating the successful conversion of ester groups in acrylate units to acrylamide in structure. Moreover, CH<sub>2</sub> peak of TEPA appeared at 46.3 ppm<sup>31</sup>, demonstrating that Cell-g-PMA-TEPA was successfully prepared.

In order to evaluate the influence of graft polymerization and subsequent amidation on surface morphology of cellulose, SEM images of cellulose, Cell-g-PMA and Cell-g-PMA-TEPA are given in Fig. 3. It can be observed that dimension of pure microcrystalline cellulose was not uniform and surface of cellulose was relatively smooth. Compared with cellulose, surface of Cell-g-PMA became rougher due to graft polymerization. After further modification with TEPA, Cell-g-PMA turned thicker and surface became much rougher due to immobilization of TEPA by amidation of acrylate groups.

#### Influence of initial pH on adsorption

It is well known that pH value of aqueous solution usually affects chelation between metal ions and chelants<sup>32</sup>. The relationship between initial pH and removal efficiency R<sub>c</sub> was studied. It can be seen that removal efficiency of Pb(II) gradually increased from 2.31% to 93.00% with an increase of pH value from 1.93 to 5.78. When pH of aqueous solution was lower than 2.5, amino groups tended to be easily protonated and the probability of interactions between Pb(II) and adsorbent (Cell-g-PMA-TEPA) was greatly reduced. Experimental results of Pb(II) adsorption denoted that Pb(II) could be easily removed from aqueous medium when pH value was adjusted to 4.5~6.

#### Adsorption kinetics

In order to study effect of contact time on Pb(II) adsorption, pseudo-first-order kinetic model and

pseudo-second-order kinetic model were used to fit experimental data to predict the process of heavy metal ions adsorption. Pseudo-first-order kinetic model could be expressed as<sup>33</sup>:

$$Q_t = Q_e (1 - e^{-k_1 t}) \quad \dots (4)$$

while pseudo-second-order kinetic model could be presented as<sup>34</sup>:

$$t/Q_t = 1/(k_2 Q_e^2) + t/Q_e \quad \dots (5)$$

where k<sub>1</sub> (min<sup>-1</sup>) and k<sub>2</sub> (g mg<sup>-1</sup> min<sup>-1</sup>) are rate constants of pseudo-first-order and pseudo-second-order model, Q<sub>t</sub> and Q<sub>e</sub> (mg g<sup>-1</sup>) are adsorption amount at time t (min) and equilibrium, respectively.

Kinetic adsorption curve of Cell-g-PMA-TEPA is shown in Fig. 4, it was observed that adsorption rate was fast at initial stage, and amount of Q<sub>t</sub> grew relatively slow during subsequent long period of time. As shown in Table 2, correlation coefficient (R<sup>2</sup>) for

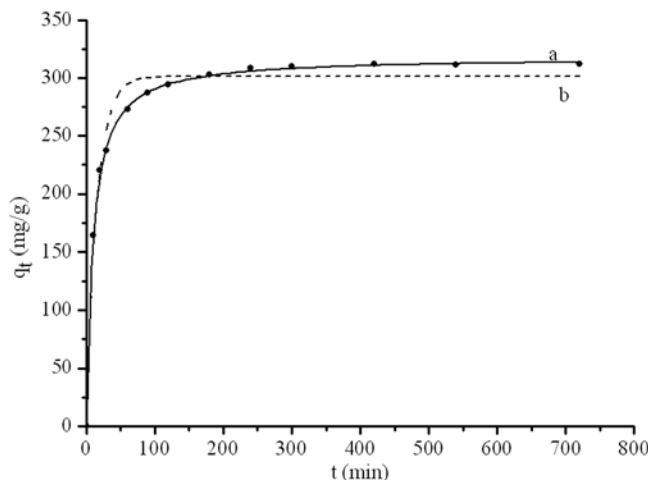


Fig. 4 — Effect of contact time on adsorbed amount of Pb(□) by Cell-g-PMA-TEPA (adsorbent: 50mg, Pb(II) solution: 30 mL), pseudo-second-order kinetic model(a), pseudo-first-order kinetic model(b)

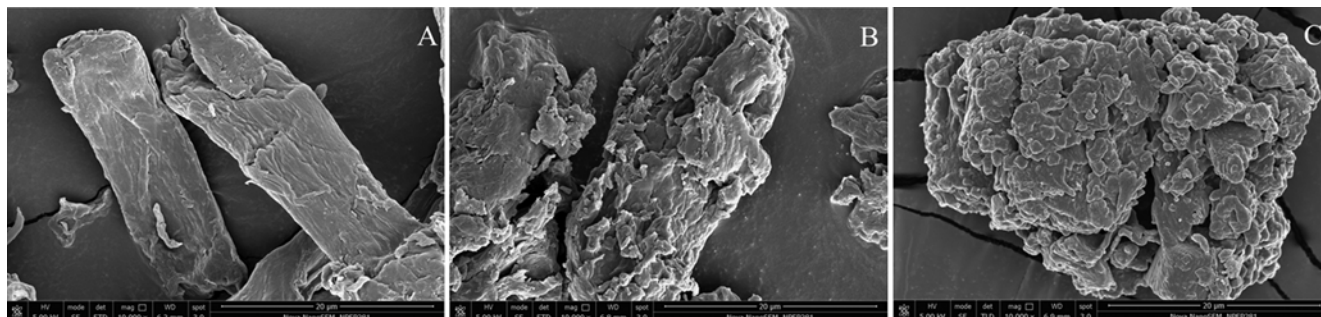


Fig. 3 — SEM images of cellulose (A); Cell-g-PMA (B) and Cell-g-PMA-TEPA (C)

pseudo-second-order model was higher than that for pseudo-first-order model, denoting that adsorption of Pb(II) may follow pseudo-second-order model<sup>35</sup>, and the process may be a chemical adsorption process involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate<sup>36</sup>.

#### Adsorption isotherms

Adsorption isotherms are usually used to describe how an adsorbate interacts with an adsorbent, and constants of isotherm models are useful in determining needed amount of adsorbent to remove specified amount of adsorbate. In this study, Langmuir and Freundlich adsorption isotherms are used to analyze adsorption experimental data.

Langmuir isotherm describes adsorption onto specific homogeneous sites within an adsorbent and can be expressed as<sup>37</sup>:

$$C_e/Q_e = 1/bQ_{\max} + C_e/Q_{\max} \quad \dots (6)$$

where  $C_e$  ( $\text{mg L}^{-1}$ ) is concentration at equilibrium,  $Q_e$  ( $\text{mg g}^{-1}$ ) is adsorbed amount of Pb(II) at equilibrium,  $Q_{\max}$  ( $\text{mg g}^{-1}$ ) and  $b$  ( $\text{L mg}^{-1}$ ) are Langmuir constants related to saturated monolayer adsorption capacity and adsorption energy. For Langmuir model, a useful parameter  $R_L$ , namely a dimensionless equilibrium parameter, can be presented as<sup>38,39</sup>:

$$R_L = 1/(1 + bC_0) \quad \dots (7)$$

where  $C_0$  ( $\text{mg L}^{-1}$ ) is initial concentration of Pb(II). The value of  $R_L$  indicates the type of isotherm to be irreversible ( $R_L=0$ ), favorable ( $0 < R_L < 1$ ), linear ( $R_L=1$ ) or unfavorable ( $R_L > 1$ ).

On the other hand, Freundlich isotherm model is based on assumption of heterogeneous surface and multilayer adsorption with an energetic nonuniform distribution, and can be defined as<sup>40</sup>:

$$\log Q_e = \log K_F + \log C_e/n \quad \dots (8)$$

Table 2— Kinetic parameters for Pb(II) adsorption by Cell-g-PMA-TEPA

Metal ion	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	$R^2$	$k_1$ ( $\text{min}^{-1}$ )	$Q_e$ ( $\text{mg g}^{-1}$ )	$R^2$	$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$Q_e$ ( $\text{mg g}^{-1}$ )
Pb(II)	0.9766	0.0645	310.2982	0.9993	0.0003	317.773

where  $K_F$  and  $n$  are Freundlich constants related to adsorption capacity and heterogeneity factor, respectively.

Linear Langmuir and Freundlich adsorption isotherms of Pb(II) ions from aqueous solution onto Cell-g-PMA-TEPA are plotted (figure not shown) to determine isotherm constants of isotherm models. The calculated values of  $b$ ,  $K_F$  and  $1/n$  have been given in Table 3. Considering value of separation factor  $R_L$  between 0 and 1, it can be assumed that adsorption process of Cell-g-PMA-TEPA for Pb(II) was favorable. It can be inferred from higher  $R^2$  values for Langmuir model that Langmuir model well fits with Pb(II) adsorption, denoting adsorption mechanism as monolayer adsorption on adsorbent surface. The performance of proposed method has been compared with some other adsorbents previously used for adsorption of Pb(II) ions and all results are listed<sup>41-47</sup> in Table 4. It can be seen that adsorption capacities of Cell-g-PMA-TEPA could be derived as  $444.4 \text{ mg g}^{-1}$  for Pb(II) in this study, much higher than those of many other adsorbents.

#### Regeneration of adsorbent

In practical application, it is also very important to regenerate and reuse adsorbent for cost-effectiveness.

Table 3—Langmuir and Freundlich parameters for Pb(II) adsorption

Metal ion	Langmuir isotherm			Freundlich isotherm		
	$R^2$	$b$ ( $\text{L mg}^{-1}$ )	$Q_{\max}$ ( $\text{mg g}^{-1}$ )	$R^2$	$K_F$	$1/n$
Pb(II)	0.9942	0.0061	444.4444	0.9865	35.0466	0.3679

Table 4—Comparison of maximum adsorption capacity for Pb(II) onto other different adsorbents

Adsorbent	Adsorption capacity $\text{mg/g}$	Reference
CPA/Cu Nanocomposite	38.93	41
CCN-g-Fe <sub>3</sub> O <sub>4</sub>	63.78	41
g-CA-TA-NMO	196.84	43
LMS	33.9	44
Cellulose/poly(ethylene imine) composites	242.8	45
CA-g-(AA-Co-AAm)	66.67	46
m-CS/PVA/CCNFS	171.0	47
Cell-g-PMA-TEPA	444.4	Present study

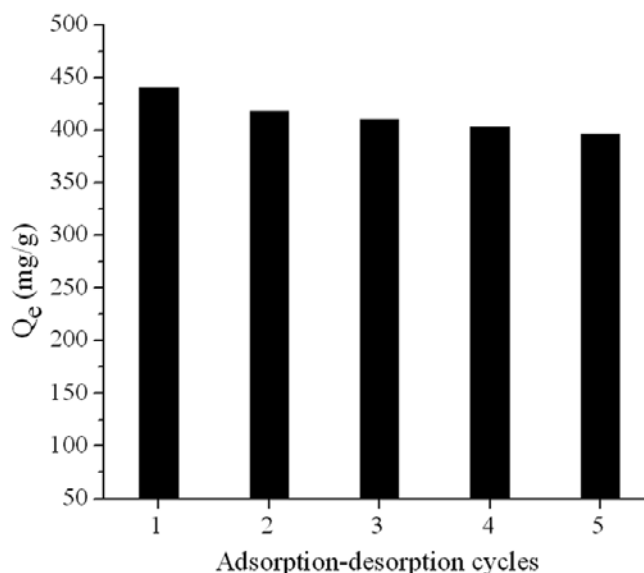


Fig. 5 — Equilibrium adsorption capacity of Cell-g-PMA-TEPA corresponding various adsorption-desorption cycles

Therefore, dynamic adsorption and desorption were performed by alternately eluting Pb(II) solution and 0.1 mol L<sup>-1</sup> HCl through adsorbent.

From Fig.5, equilibrium adsorption capacity after first adsorption-desorption cycle was 440.4 mg g<sup>-1</sup>, slightly less than maximum adsorption capacity derived from Langmuir isotherm. There has been less than 10% in loss of adsorption capacity for Pb(II) after five adsorption-desorption cycles, proving fairly satisfactory reusability of prepared adsorbent for removal of Pb(II) from aqueous solution.

## Conclusion

In this study, Cell-g-PMA-TEPA, an efficient adsorbent for Pb(II) is successfully prepared, which can be verified by characterization as elemental analysis, FT-IR, solid-state <sup>13</sup>C-NMR and SEM. Adsorption process follows pseudo-second-order kinetic model and adsorption isotherms fit well with Langmuir model, from which maximum adsorption capacity could be derived as high as 444.4 mg g<sup>-1</sup>. Further dynamic adsorption experiments reveal that adsorbent can be regenerated and there is not been much loss in equilibrium adsorption capacity after five adsorption-desorption cycles.

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