Hydrazinolyzed cellulose-g-polymethyl acrylate as adsorbent for efficient removal of Cd(II) and Pb(II) ions from aqueous solution

Qiujin Jia, Wanting Zhang, Dongping Li, Yulong Liu, Yuju Che, Qinglin Ma and Fanjun Meng

ABSTRACT

Hydrazinolyzed cellulose-g-polymethyl acrylate (Cell-g-PMA-HZ), an efficient adsorbent for removal of Cd(II) and Pb(II) from aqueous solution, has been prepared by ceric salt-initiated graft polymerization of methyl acrylate from microcrystalline cellulose surface and subsequent hydrazinolysis. The influences of initial pH, contact time, and temperature on adsorption capacity of Cell-g-PMA-HZ as well as adsorption equilibrium, kinetic and thermodynamic properties were examined in detail. As for Cd(II) adsorption, kinetic adsorption can be explained by pseudo-second-order, while adsorption isotherm fits well with Langmuir isotherm model, from which maximum equilibrium adsorption capacity can be derived as 235.85 mg g\(^{-1}\) at 28°C. Further thermodynamic investigation indicated that adsorption of Cd(II) by adsorbent Cell-g-PMA-HZ is endothermic and spontaneous under studied conditions. On the other hand, isotherm of Pb(II) adsorption fits well with Freundlich isotherm model and is more likely to be a physical-adsorption-dominated process. Consecutive adsorption-desorption experiments showed that Cell-g-PMA-HZ is reusable with satisfactory adsorption capacity.

Key words | adsorption, cadmium(II), cellulose, hydrazinolyzed cellulose-g-polymethyl acrylate (Cell-g-PMA-HZ), lead(II)

INTRODUCTION

Cadmium (Cd) and lead (Pb) ions, part of the most toxic heavy metal ions to human health, originate as contaminants from processes including electroplating, mining, plastics, paint pigments, alloy preparation and silver-cadmium batteries (Zheng et al. 2010). Once their lower concentration thresholds are exceeded, cadmium and lead ions will affect health and cause serious diseases such as renal dysfunction, hypertension, lung failure, bone lesions and cancer (Sun et al. 2014). Based on the above facts, more and more attention has been paid to the development of advanced technologies for reducing cadmium and lead ions in the human environment.

Traditionally, several methods have been utilized to remove cadmium and lead ions from aqueous solution, including reverse osmosis, chemical precipitation, ion exchange and electrochemical treatment (Peng et al. 2012). However, these methods have some limitations, such as high cost, low efficiency and possible secondary contamination. Recently, adsorption has been proved to be one of the most effective strategies for removal of heavy metal ions such as Cd(II) and Pb(II) (Bailey et al. 1999; Leyva-Ramos et al. 2005), and versatile adsorbents have been developed; the corresponding adsorption mechanism has also been well investigated (O’Connell et al. 2008a, 2008b). Since biomaterials such as cellulose and chitosan are renewable, biodegradable, cheap and available in large amounts, easier to be separated from treated solution through sedimentation and filtration, graft polymerization of vinyl monomers from biomaterial and subsequent modification with chelating reagents has recently become an attractive method to develop efficient adsorbents for heavy metal ions (Zhou et al. 2004; Saber-Samandari et al. 2014). For example, a new biosorbent has been prepared through graft polymerization of acrylonitrile from Iranian tragacanth gum (ITG) and subsequent amidoximation with hydroxyamine.
hydrochloride by Masoumi and Mousa Ghaemy (Masoumi & Ghaemy 2014), affording maximum adsorption capacities \(q_m\) as 100.0, 76.92, 71.42 and 66.67 (mg g\(^{-1}\)) derived from Langmuir adsorption isotherms for adsorption of some heavy metal ions in the order of Co(II) > Zn(II) > Cr(III) > Cd(II). Although it has been less reported (Johari et al. 2013a, 2013b), functionalized cellulose-graft-poly (methyl acrylate) can also be applied for adsorption of heavy metal ions, yet mainly for Cu(II) and Ni(II) adsorption. In previous work, hydrazinolyzed cellulose-graft-poly (methyl acrylate) (Cell-g-PMA-HZ) has been prepared and indicated greatly improved adsorption capacities for Cu(II) and Ni(II) ions in our laboratory, and maximum equilibrium adsorption capacity can be increased to 229.36 mg g\(^{-1}\) for Cu(II) and 173.91 mg g\(^{-1}\) for Ni(II) at 28 °C (Jia et al. 2016) due to high grafting percentage and high degree of hydrazinolysis. The reason why we use expensive, potentially toxic compounds such as ceric salts and hydrazine mainly lies in two aspects. On the one hand, the grafting yield for ceric salt-initiated graft polymerization is apparently higher than that for graft polymerization initiated by other initiators such as benzoyl peroxide (BPO), 2,2’-azobisisobutyronitrile (AIBN), ammonium persulfate (APS), potassium persulfate (KPS) and potassium permanganate, which has been verified in our laboratory. On the other hand, the low cost of the preparation method and high sustainable capability make the actual cost much lower than it seems. Considering the more serious harmfulness to the human body resulting from Cd(II) and Pb(II) as well as possible application in adsorption for other heavy metal ions, in this study, we continued to study the adsorption behavior of Cell-g-PMA-HZ for Cd(II) and Pb(II) in aqueous solution.

**MATERIALS AND METHODS**

Reagent grade microcrystalline cellulose (average particle diameter 25 μm), analytical grade methyl acrylate (MA), ceric ammonium nitrate (CAN) and hydrazine hydrate (80%) were purchased from Aladdin Reagent (China). The Cd(II) and Pb(II) standard solutions were commercially available (National Analysis Center of Iron and Steel, China). All reagents were used as received except that MA was distilled under reduced pressure before graft polymerization. Hydrazinolyzed cellulose-graft-poly(methyl acrylate) Cell-g-PMA-HZ was prepared through grafting MA from microcrystalline cellulose with CAN as initiator in aqueous medium according to the method described before (Gupta et al. 2002) and subsequent hydrazinolysis of attained cellulose-graft-poly (methyl acrylate) (Cell-g-PMA) (of 320% grafting percentage) with 80% hydrazine in ethanol. The hydrazinolysis mixture was stirred for 3 h at 55 °C and then filtered, rinsed with deionized water and further dried at 60 °C under reduced pressure until constant weight (Jia et al. 2016).

The successful synthesis of cellulose derivatives was confirmed using Fourier-transform infrared spectrometer (FT-IR, Vertex70, Bruker Co., Germany), NMR spectrometer (NMR, Avance III 400M, Bruker Co., Germany), elemental analyzer (Vario EL III, Elementar, Germany) and scanning electron microscope (Nova NanoSEM NPEP281). Concentrations of heavy metal ions in solution were determined by a flame atomic adsorption spectrophotometer (AAS, novAA300/400FL, Analytic Jena AG Co., Germany) as mean values of four replicates reported (RSD < 3%).

Batch equilibrium tests were carried out for adsorption of Cd(II) and Pb(II) ions on prepared adsorbent. The metal ion solutions were prepared by dissolving specified weights of metal salts in 250 mL of distilled water. The pH of metal ion solution was adjusted with dilute HNO\(_3\) or NaOH solutions. The prepared adsorbent samples were introduced into stoppered Erlenmeyer flasks together with metal salt solution of specified initial concentration. The flasks were fixed in a temperature-controlled shaker, adsorption experiments were carried out at preset temperatures for specified time intervals, and equilibrium adsorption capacity \(q_e\) was calculated according to the following equation (Equation (1)): (An et al. 2011)

\[
q_e = \frac{V(C_0 - C_e)}{m}
\]

where \(C_0\) and \(C_e\) are initial and equilibrium concentration of heavy metal ions, respectively; \(q_e\) is equilibrium adsorption capacity, i.e., adsorbed amount of heavy metal ions onto per gram of adsorbent (mg g\(^{-1}\)); \(V\) is the volume of aqueous solution (L); and \(m\) is the mass of adsorbent (g).

**RESULTS AND DISCUSSION**

Verification of successful graft polymerization of methyl acrylate and hydrazinolysis of thus prepared Cell-g-PMA can be referred to previous characterization (Jia et al. 2016).

**Effect of initial pH on metal ion adsorption**

Since heavy metal ions and chelating groups might exhibit different chemical properties under acidic and basic
conditions, pH value of the metal ion solution plays an important role in controlling uptake of metal ions by adsorbent (Figure 1). To study the influence of pH value of Cd(II) and Pb(II) solution on adsorption capacity of Cell-g-PMA-HZ, adsorption experiments were carried out at a pH range of 2.0–6.0. It is clear from Figure 2 that adsorption capacities of Cell-g-PMA-HZ for Cd(II) and Pb(II) increased as pH values of metal ion solutions increased. The lower uptake of Cd(II) and Pb(II) (at pH 2) may be attributed to competition of Cd(II) or Pb(II) and protons with protonated hydrazino groups, which leads to strong electrostatic repulsion. As pH increases, hydrazides on adsorbent surface turn into dissociated forms, giving a greater number of nucleophilic binding sites. As the solution pH increased to pH 6, the adsorption capacity was found to decrease due to the formation of cadmium or lead hydroxide in solution (Guo et al. 2014).

**Kinetic adsorption curve**

In order to clarify the adsorption process, kinetic models such as pseudo-first-order and pseudo-second-order were applied to evaluate experimental data. The equations can be written in the forms (Liu et al. 2009):

\[ q_t = q_e \left(1 - e^{-k_1 t}\right) \]  
\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \]  

where \( q_t \) and \( q_e \) are the amount of heavy metal ions adsorbed at time \( t \) and at equilibrium (mg g\(^{-1}\)), and \( k_1 \) and \( k_2 \) are apparent adsorption rate constants for first-order and second-order models (min\(^{-1}\) and mg g\(^{-1}\) min\(^{-1}\)).

The kinetic adsorption curves of Cell-g-PMA-HZ for Cd(II) and Pb(II) are shown in Figure 3, showing that adsorption capacity for Cd(II) and Pb(II) in the experimental period fits better with a pseudo-second-order model (solid line) than with a pseudo-first-order model (dotted line). Kinetic parameters for either model were calculated by non-linear regression analysis using the ORIGIN program, Version 9.0, and the results are given in Table 1. The experimental results could be well described by a pseudo-second-order equation for adsorption of both metal ions studied. Validity of the model could be qualified by the good correlation coefficient \( R^2 > 0.99 \). Moreover, it can also be noticed that calculated adsorption capacity at equilibrium \( (q_e, \text{cal}) \) from the pseudo-second-order kinetic model generally deviates less from experimental adsorption capacity at equilibrium \( (q_e, \text{exp}) \), which suggests that the adsorption under investigation may follow a chemical adsorption process involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate.

![Figure 1](https://iwaponline.com/wst/article-pdf/75/5/1051/454484/wst075051051.pdf)
Equilibrium adsorption was performed to provide capacity of the adsorbent, and experimental adsorption data were applied to fit Langmuir and Freundlich isotherm models, respectively. The Langmuir model suggests an estimation that maximum adsorption capacity occurs through complete monolayer adsorption on the adsorbent surface, while the Freundlich model allows for several kinds of adsorption sites on a solid surface and represents properly the adsorption data at low and intermediate concentrations on heterogeneous surfaces (Zheng et al. 2017; TAlooki et al. 2012; Fathi et al. 2015). Linear Langmuir and Freundlich equations can be expressed as Equations (4) and (5).

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L}
\]

\[
\ln q_e = \frac{1}{n} \ln C_e + \ln K_F
\]

where \(q_e\) (mg g\(^{-1}\)) and \(C_e\) (mg L\(^{-1}\)) are amount (mg) of adsorbed metal ions per unit weight (g) of adsorbent and metal ion concentration in solution at equilibrium; \(K_L\) (L mg\(^{-1}\)) is the Langmuir constant relating to free energy of adsorption; \(q_m\) is maximum adsorption capacity of adsorbent. \(K_F\) [(mg g\(^{-1}\))(L mg\(^{-1}\))\(^{1/n}\)] and \(n\) are isotherm constants, which indicate capacity and intensity of adsorption.

Adsorption isotherm constants were determined using linear regression analysis, and the results are given in Table 2. Considering higher \(R^2\) values for the Langmuir model at all temperatures studied, Cd(II) adsorption isotherm data fit with the Langmuir model better than the Freundlich model, indicating that the adsorption process for Cd(II) by Cell-g-PMA-HZ is more likely monolayer adsorption, and maximum equilibrium adsorption capacity can be derived as 235.85 mg g\(^{-1}\) at 28°C. And the adsorption capacity is found to increase with increase in temperature, indicating the endothermic nature of the adsorption process. The value of \(K_L\), relating to the binding energy, also increases along with the temperature’s growth, suggesting contribution of stronger binding sites at higher temperature conditions. As temperature increases, the weaker binding sites are occupied first, and that binding

<table>
<thead>
<tr>
<th>Heavy metal ions</th>
<th>(q_{e,exp}) (mg g(^{-1}))</th>
<th>Model</th>
<th>(R^2)</th>
<th>(q_{e,cal}) (mg g(^{-1}))</th>
<th>(k_1) (min(^{-1}))</th>
<th>(k_2) (g mg(^{-1})min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(II)</td>
<td>230.35</td>
<td>Pseudo-first-order kinetic model</td>
<td>0.9837</td>
<td>216.71</td>
<td>0.03727</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pseudo-second-order kinetic model</td>
<td>0.9989</td>
<td>232.29</td>
<td>–</td>
<td>2.5923*10(^{-4})</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>118.67</td>
<td>Pseudo-first-order kinetic model</td>
<td>0.9872</td>
<td>105.18</td>
<td>0.02831</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pseudo-second-order kinetic model</td>
<td>0.9927</td>
<td>114.28</td>
<td>–</td>
<td>3.1932*10(^{-4})</td>
</tr>
</tbody>
</table>
strength increases with increasing degree of site occupation. On the other hand, Pb(II) adsorption isotherm data fit with the Freundlich model better, and the n value means a heterogeneous nature of the Cell-g-PMA-HZ characterized by an exponential distribution of adsorption sites. The values of 1/n fall in the range of 0–1, which means that the sorption intensity is favorable at relatively high concentration but much less so at lower concentration (Guo et al. 2014; Jin et al. 2014). It was indicated that adsorption for Pb(II) on Cell-g-PMA-HZ was non-ideal adsorption on heterogeneous surfaces and might be a physical process favorable under the experimental conditions used in the study.

Moreover, the performance of our proposed adsorbent used for removal of Cd(II) and Pb(II) has been compared with previous biomaterial-based adsorbents, and the results of the comparison, shown in Table 3, indicate much

<table>
<thead>
<tr>
<th>Absorbents</th>
<th>q_m (mg g⁻¹) for Cd(II)</th>
<th>q_e (mg g⁻¹) for Pb(II)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugarcane bagasse (MSB) grafted acrylonitrile</td>
<td>14.28</td>
<td>–</td>
<td>Niu et al. (2014)</td>
</tr>
<tr>
<td>Stalk grafted acrylonitrile copolymer (AGCS)</td>
<td>22.17</td>
<td>–</td>
<td>Zheng et al. (2010)</td>
</tr>
<tr>
<td>Cellulose-g-GMA-imidazole</td>
<td>–</td>
<td>71.00</td>
<td>O’Connell et al. (2008a, 2008b)</td>
</tr>
<tr>
<td>Carboxylic acid functionalized deacetylated konjac glucomannan</td>
<td>–</td>
<td>117.10</td>
<td>Liu et al. (2009)</td>
</tr>
<tr>
<td>Nanohydrogel tragacanth gum-g-polyamidoxime (ITG-g-PAO)</td>
<td>66.67</td>
<td>–</td>
<td>Masoumi &amp; Ghaemy (2014)</td>
</tr>
<tr>
<td>EGTAD dianhydride (EGTAD) modified ramie fiber</td>
<td>159.11</td>
<td>149.39</td>
<td>Sun et al. (2014)</td>
</tr>
<tr>
<td>Poly(methacrylic acid-co-maleic acid) grafted nanofibrillated cellulose</td>
<td>233.81</td>
<td>–</td>
<td>Maatar &amp; Boufi (2015)</td>
</tr>
<tr>
<td>Cell-g-PMA-HZ</td>
<td>235.85</td>
<td>249.89</td>
<td>This study</td>
</tr>
</tbody>
</table>

Figure 4 | Van’t Hoff plot of lnK_p versus 1/T.
higher adsorption capacities of Cell-g-PMA-HZ for Cd(II) and Pb(II) than those of many other adsorbents. It should be noted that, instead of maximum adsorption capacity, $q_m$, for Cd(II) adsorption, equilibrium adsorption capacity, $q_e$, for Pb(II) adsorption was given in Table 3, since $q_m$ was unable to be derived from the Freundlich model.

Thermodynamic study

The effect of temperature on adsorption isotherms has been investigated under isothermal conditions in a temperature range of 28°C–58°C. The thermodynamic parameters of adsorption, i.e., standard free energy changes ($\Delta G^0$, kJ mol$^{-1}$), standard enthalpy changes ($\Delta H^0$, kJ mol$^{-1}$) and standard entropy changes ($\Delta S^0$, kJ mol$^{-1}$K$^{-1}$) were calculated from the temperature dependent adsorption isotherms using classical thermodynamic equations (Chauhan et al. 2006; Anirudhan & Senan 2011):

$$\ln K_p = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

(6)

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

(7)

where $K_p$ is the thermodynamic equilibrium constant, which can be determined by plotting $\ln(q_e/C_0)$ versus $q_e$ and extrapolating to zero $q_e$. Figure 4 shows the Van ‘t Hoff plot of $\ln K_p$ versus $1/T$ with T as absolute temperature, based on which $\Delta H^0$ and $\Delta S^0$ can be derived from slope and intercept, respectively. Consequential thermodynamic parameters are listed in Table 4. From Table 4, the positive $\Delta H^0$ value indicated that the adsorption reaction for adsorbing Cd(II) onto the adsorbent was an endothermic process, which is supported by the result that adsorption capacity of Cell-g-PMA-HZ for Cd(II) will increase with increasing temperature. The positive value of $\Delta S^0$ reflected the affinity of the Cell-g-PMA-HZ substance fractions towards Cd(II) and the increase of degree of freedom at the solid/liquid interface during the adsorption process. The negative $\Delta G^0$ values at all temperatures indicated the feasibility and spontaneous nature of the adsorption of Cd(II) on Cell-g-PMA-HZ, which means that the adsorptive force is strong enough to break the potential and lead the reaction to bind Cd(II) onto the surface functional groups of Cell-g-PMA-HZ. The decrease in $\Delta G^0$ values with increase in temperature implied that the adsorption reaction was more favorable at higher temperature. On the other hand, unlike Cd(II) adsorption, Pb(II) adsorption shows negative values for $\Delta H^0$ and $\Delta S^0$. The above fact indicates two aspects, as follows. On the one hand, corresponding to the increasing $\Delta G^0$ values caused by increasing temperatures, the adsorption of Pb(II) onto the adsorbent was exothermic and dominated by a physical sorption process ($|\Delta H^0| < 20$ kJ mol$^{-1}$) (Niu et al. 2014). On the other hand, the degree of freedom at the solid-liquid interface during the adsorption process was decreasing.

Reusability

Good reusability of an adsorbent is essential for its practical applications, and adsorption-desorption cycles have been carried out to evaluate recovery of adsorbent Cell-g-PMA-HZ by a dynamic adsorption method. To regenerate the adsorbent, 1.0M HCl was introduced to elute through

Table 4 | Thermodynamic parameters for Cd(II) and Pb(II) adsorption

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta S$ (kJ mol$^{-1}$K$^{-1}$)</th>
<th>28°C</th>
<th>38°C</th>
<th>48°C</th>
<th>58°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(II)</td>
<td>27.4245</td>
<td>0.1001</td>
<td>-2.6973</td>
<td>-3.7810</td>
<td>-4.7709</td>
<td>-5.6989</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>-5.4230</td>
<td>-0.0164</td>
<td>-0.4948</td>
<td>-0.3312</td>
<td>-0.1676</td>
<td>-0.0039</td>
</tr>
</tbody>
</table>

Figure 5 | Regeneration of Cell-g-PMA-HZ (adsorbent: 100 mg, temperature: 28°C, initial concentration of Cd(II) and Pb(II): 1,000 mg L$^{-1}$, pH: 5.0).
adsorbent saturated with Cd(II) or Pb(II). As shown in Figure 5, the adsorbent was found to maintain 84.5% and 86.2% of its original sorption capacity for Cd(II) and Pb(II), respectively, after six cycles of adsorption-desorption, showing comparable reusability to other studies in the references (listed in Table 5).

**CONCLUSION**

In the present study, the potential of Cell-g-PMA-HZ as an adsorbent for adsorption of Cd(II) and Pb(II) from aqueous solutions was investigated. Factors affecting adsorption of heavy metal ions, such as initial pH, contact time and temperature, have been extensively investigated. Kinetic adsorption of Cell-g-PMA-HZ for both Cd(II) and Pb(II) can be explained by a pseudo-second-order model. Furthermore, adsorption isotherms for Cd(II) adsorption fit well with the Langmuir isotherm model, from which maximum equilibrium adsorption capacity can be derived as 235.85 mg g⁻¹ at 28 °C, while adsorption isotherms for Pb(II) adsorption fit better with the Freundlich model. Thermodynamic data indicated that adsorption of Cd(II) onto Cell-g-PMA-HZ is endothermic and spontaneous, while adsorption of Pb(II) onto adsorbent is exothermic and spontaneous, denoting that the adsorption process for Pb(II) ions probably undergoes non-ideal adsorption on heterogeneous surfaces or multilayer adsorption dominated by a physical adsorption process. Dynamic adsorption and desorption experiments also revealed that Cell-g-PMA-HZ is reusable following efficient recovery of Cd(II) and Pb(II) when dilute hydrochloric acid (1 mol L⁻¹) was employed as eluent.

**REFERENCES**


Anirudhan, T. S. & Senan, P. 2011 Adsorptive characteristics of chromium (VI) ions from aqueous phase by iron (III) coordinated amino-functionalized poly(glycidyl methacrylate)-grafted cellulose: equilibrium kinetics and thermodynamic study. *Separation Science and Technology* **46** (9), 1430–1442.


graphenes composite material and its application to remove Cr (VI), Pb (II), Hg (II), Cd (II) and Ni (II) from contaminated water. *Journal of Hazardous Materials* **278**, 211–220.


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