Facile preparation of low-cost HKUST-1 with lattice vacancies and high-efficiency adsorption for uranium

Aili Yang, Ping Li and Jingrong Zhong

In this work, we prepared HKUST-1 and HKUST-1 with lattice vacancies (HLV) using benzoic acid (BA) as a low-cost modulator to replace part of the traditional trimesic acid ligand (H$_3$BTC). The structure and morphology of the products were characterized by FTIR, XRD, SEM and XPS. The adsorption performance of the products for uranium from aqueous solutions was investigated. The results showed that the sorption of U(VI) on HKUST-1 and HLV agreed with the Langmuir isotherm model ($R^2_{\text{HKUST-1}} = 0.9867$ and $R^2_{\text{HLV}} = 0.9828$) and the maximum adsorption capacity was 430.98 mg g$^{-1}$ and 424.88 mg g$^{-1}$, respectively. According to kinetics studies, the adsorption fitted better with a pseudo-second-order model ($K_{\text{ads}}$ = 1.000 and $R^2_{\text{HLV}} = 0.9978$). The as-prepared adsorbents were used for the removal of uranium from real water samples as well. The results showed that HLV with lower cost is a promising adsorbent for uranium from aqueous solutions.

1. Introduction

Nowadays, there is a growing interest in the development and applications of various nanostructured materials in many fields. Various materials including organic complexes, inorganic nanocomposites, and polyzwitterions/anions have been applied for contamination removal. Recently, metal-organic frameworks (MOFs) have become a new promising nanostructured material. MOFs are crystalline porous materials comprised of metal ions linked by various organic bridges. MOFs with large specific surface areas, high porosity, tuneable pore sizes and adjustable internal surfaces have been widely applied in various fields, such as gas storage and separation, catalysis, supercapacitor fabrication and adsorption of undesirable materials. Among various wastewater treatment technologies adsorption is considered the best and most universal technique for the removal of a wide variety of organic and inorganic pollutants. Because of its excellent chemical and thermal stability, HKUST-1 is a typical material among MOFs and has been intensively investigated for the removal of various pollutants, such as H$_2$S, Pb(II), dyes, Sr$^{2+}$, Ni(II), As(V), Cr(VI), hydroquinone, fluoroquinolone, pesticides and uranium.

In general, trimesic acid (H$_3$BTC) has been used as the traditional ligand to prepare HKUST-1 in the previous reports. However, the cost of H$_3$BTC (the cost of analytical grade product is currently 566 ¥/500 g) is much higher than that of benzoic acid (BA) with less COOH groups (the cost of analytical grade product is currently 16.4 ¥/250 g). The preparation cost of HKUST-1 will greatly reduce by using BA as the ligand to replace part of H$_3$BTC. To the best of our knowledge, no reports have been published about the preparation and adsorption capacity of HKUST-1 using low-cost BA as the modulator for uranium from aqueous solutions. Therefore, to reduce significantly the preparation cost of HKUST-1, we used BA to replace part of the traditional H$_3$BTC ligand to obtain HKUST-1 with lattice vacancies (HLV). Moreover, the as-synthesized HKUST-1 and HLV in the present work have another two advantages: (1) the removal rate of uranium using HKUST-1 and HLV reached 99% even for the solutions bearing a high concentration of uranium (100 mg L$^{-1}$), and (2) the maximum adsorption capacity of HKUST-1 and HLV were up to about 431 and 425 mg g$^{-1}$, respectively, which was higher than most of the reported references (see Table 3). Herein, we prepared HKUST-1 and HLV by a simple hydrothermal synthesis method for the adsorption of uranium from aqueous solutions. The influence of solution pH, co-existing ions, contact time, and initial U(VI) concentration on the adsorption capacity was studied. The adsorption isotherms and kinetics models were also investigated.

2. Materials and methods

2.1. Materials

Stock solutions of uranium (5–100 mg L$^{-1}$) were prepared by dissolving UO$_2$(NO$_3$)$_2$·6H$_2$O (Xi’an Dingtian Chemical Reagent Co.) in deionized water (DW) and acidified with a small amount of concentrated HNO$_3$. All the chemicals, i.e., Cu(NO$_3$)$_2$·3H$_2$O, H$_3$BTC, BA and absolute ethanol, were of analytical grade and used without further purification. DW was used throughout the experiments.
2.2. Preparation of HKUST-1 and HLV

The preparation method of HKUST-1 and HLV was modified according to the ref. 31. In a typical synthesis of HKUST-1, 1.0870 g of Cu(NO₃)₂·3H₂O was dissolved in 15 ml DW, while 0.5250 g of H₃BTC was dissolved in 15 ml absolute ethanol. Both solutions were mixed and stirred for 30 min. The resulting mixture was transferred into a Teflon autoclave and heated in an oven at 110 °C for 24 h. The resultant blue crystals were filtered under vacuum and washed with ethanol and DW (v : v = 1 : 1) and ethanol. Then, the products were immersed in ethanol for 36 h and ethanol was replaced every 12 h. Finally, the products were filtered under vacuum and dried at 100 °C under vacuum.

In a typical synthesis of HLV, 1.0870 g of Cu(NO₃)₂·3H₂O was dissolved in 15 ml DW. The mixture of H₃BTC and BA with molar ratio 3 : 1 was dissolved in 15 ml absolute ethanol. Then, both solutions were transferred into a Teflon autoclave and heated in an oven at 110 °C for 24 h. The resultant blue crystals were filtered under vacuum and washed with a solution of ethanol and DW (v : v = 1 : 1) and ethanol. Then, the products were immersed in ethanol for 36 h and ethanol was replaced every 12 h. Finally, the products were filtered under vacuum and dried at 100 °C under vacuum.

2.3. Characterization of the products

The Fourier transform infrared (FTIR) spectra of the as-prepared adsorbents were obtained using an FTIR spectrometer (Bruker VERTEX 70, Germany). The crystal phases of the samples were characterized by X-ray diffraction (XRD) pattern (Dandong Fangyuan DX-2700 model, China). The surface morphology of the products was determined using scanning electron microscopy (SEM) (FEI Helios 600i, USA). X-ray photoelectron spectroscopy (XPS) was used to analysis the elemental content of HKUST-1 and HLV using an ESCALAB 250 X-ray photoelectron spectrometer (Thermo Fisher, USA).

2.4. Adsorption tests

The influences of pH, contact time and initial uranium concentration on the removal efficiency of uranium were investigated by batch adsorption experiments. The solution pH was adjusted by NaOH and HCl. The as-prepared adsorbent was added to a 20 ml U(vi) solution and shaken in a shaker (Kangshi, China). After filtration, residual uranium concentrations were measured by a micro-quantity uranium analyser (MUA model, China). The removal rate \( R(\%) \) and the adsorption capacity of U(vi) \( Q (\text{mg g}^{-1}) \) were calculated according to eqn (1) and (2), respectively.

\[
R(\%) = \frac{c_0 - c_t}{c_0} \times 100 \tag{1}
\]

\[
Q (\text{mg g}^{-1}) = \frac{(c_0 - c_t)}{W} \times V \tag{2}
\]

where \( c_0 (\text{mg L}^{-1}) \) is the initial U(vi) concentration, \( c_t (\text{mg L}^{-1}) \) is U(vi) concentration at time \( t \), \( V (\text{L}) \) is the solution volume and \( W (\text{g}) \) is the weight of adsorbent.

3. Results and discussion

3.1. Characterization of the products

The functional group structures of HKUST-1 and HLV were determined by FTIR and are shown in Fig. 1. The characteristic peak at 1370 cm\(^{-1}\) was assigned to the C–O of H₃BTC, and the bands at 1448 cm\(^{-1}\) and 1549 cm\(^{-1}\) were attributed to the C=O of H₃BTC. The characteristic peak at 1647 cm\(^{-1}\) resulted from aromatic C=C of H₃BTC. This result is in accordance with a previous study.\(^{31,32}\) However, in the HLV FTIR spectrum, the intensity of the H₃BTC characteristic peaks at 1448 cm\(^{-1}\) and 1549 cm\(^{-1}\) attributed to C=O and the –COOH group at >3000 cm\(^{-1}\) decreased significantly because part of the H₃BTC was replaced by BA in the HLV, which has fewer –COOH groups than H₃BTC. Moreover, by XPS elemental analysis the calculated atomic ratio of C : Cu : O in HKUST-1 and HLV is 8.37 : 1 : 4.73 and 7.22 : 1 : 4.25, respectively, which indicated that the part of H₃BTC was replaced by BA with less –COOH groups in HLV.

The XRD patterns of the resulting HKUST-1 and HLV are shown in Fig. 2. All of the diffraction peaks of HKUST-1 were in accordance with those reported in the ref. 29, and the indexed values of all of the diffraction peaks were accordane with the reference.\(^{31–35}\) Fig. 2 shows that the crystalline structure of HKUST-1 was similar to that of HLV. No obvious impurity peaks can be detected in the XRD patterns of HKUST-1 and HLV. The results showed that HKUST-1 and HLV had good chemical
stability and high crystallinity even if the part of H$_2$BTC was replaced by BA.

The morphology of HKUST-1 and HLV are shown in Fig. 3. In the SEM of HKUST-1, the crystal sizes of tens of microns (Fig. 3a) were observed. Some of the particles were octahedra with clear edges, and the other particles were flower-like (Fig. 3b). Due to the replacement by BA, the pores in HLV were deeper than those in HKUST-1.

### 3.2. Effect of pH and co-existing ions on adsorption

The adsorption of U(Ⅵ) by HKUST-1 and HLV as a function of pH was carried out over the pH range of 3.0–8.0 for 30 min, as shown in Fig. 4, and the effect of co-existing ions on U(Ⅵ) adsorption was shown in Fig. 4 (inset). The results showed a significant impact of pH on uranium adsorption. The highest removal rate of U(Ⅵ) was observed at pH 4.0 and was found to be nearly 100%. The observed lower removal efficiency of U(Ⅵ) at pH < 3 may be attributed to formation of repulsive force between the protonated adsorbent and the positively charged uranyl ions which hindered the mass transfer and their adsorption onto the adsorbent. With the increase of pH, deprotonation of HKUST-1 and HLV cause enhance in the complex formation and improvement in mass transfer to the adsorbent surface. However, at pH > 5 the interaction of U(Ⅵ) with HKUST-1 and HLV decreased due to the formation of uranyl species with low adsorption affinities, such as [UO$_2$OH]$^-$, [(UO$_2$)$_3$(OH)$_4$]$^{2+}$, [(UO$_2$)$_3$(OH)$_5$]$^+$, [(UO$_2$)$_2$(OH)$_2$]$^{2+}$, [(UO$_2$)$_2$OH]$^{3+}$, [(UO$_2$)$_3$(OH)]$^5^+$, and [(UO$_2$)$_4$(OH)]$^7^+$. Therefore, the optimum pH of HKUST-1 and HLV for U(Ⅵ) adsorption was 4.0. Moreover, the effect of co-existing ions (K$^+$, Mg$^{2+}$, Ca$^{2+}$, Al$^{3+}$ and Sr$^{2+}$) on U(Ⅵ) sorption is examined. As shown in Fig. 4 (inset), some co-existing ions (such as Mg$^{2+}$ and Ca$^{2+}$) had significantly effect on the adsorption efficiency for U(Ⅵ) by HLV at pH 4 while some ions (such as Al$^{3+}$ and Sr$^{2+}$) had no effect on the adsorption efficiency for U(Ⅵ).

### 3.3. Influence of contact time and adsorption kinetics study

Fig. 5a shows the effect of contact time on uranium adsorption by HKUST-1 and HLV. The adsorption efficiency of HKUST-1
Table 1 Parameters of pseudo-first-order and pseudo-second-order kinetic models for U(Ⅵ) adsorption by HKUST-1 and HLV. pH = 4.0, C_{U\text{initial}} = 10 mg L⁻¹, m/V = 0.25 g L⁻¹

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Qₐ (mg g⁻¹)</th>
<th>k₁ (min⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>HKUST-1</td>
<td>0.5492</td>
<td>0.0014</td>
<td>0.0428</td>
</tr>
<tr>
<td>HLV</td>
<td>4.2973</td>
<td>0.0191</td>
<td>0.4827</td>
</tr>
</tbody>
</table>

Qₐ = Qₘk₁Cₑ/(1 + k₁Cₑ)

where Qₑ (mg g⁻¹) is the equilibrium adsorption capacity, Cₑ (mg L⁻¹) is the uranium concentration at equilibrium, Qₘ (mg g⁻¹) is the maximum adsorption capacity, k₁ (L mg⁻¹) and k₂ (g (mg⁻¹ min⁻¹)) are the Langmuir constant and Freundlich constant, respectively, and n is the Freundlich adsorption exponent.

A comparison of Qₘ of HKUST-1 and HLV in this work and the reported other adsorbents is presented in Table 3. Table 3 shows that as-prepared low-cost HLV had higher Qₘ than most of the reported adsorbents and proved to be a promising adsorbent for the treatment of uranium-bearing wastewater.

3.5. Adsorption efficiency for real wastewater samples
Under the optimum adsorption conditions, the removal efficiency of U(Ⅵ) by HKUST-1 and HLV for low-level uranium-
bearing real wastewater from five different batches was evaluated. Some micro-quantity metal ions (e.g., Al, B, Ca, Be, Fe, Cu, Mn, Mg, Si, Ni and Mo) were found to exist in the real wastewater samples. All elements in real samples were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Thermo Fisher iCAP 6300, USA). The adsorption experiments results are presented in Fig. 7. As shown in Fig. 7, HKUST-1 and HLV had favourable adsorption capacity for high-level uranium-bearing wastewater (≥1.0 mg L\(^{-1}\)), and the co-existing ions had no effect on the removal efficiency for uranium. However, the uranium concentration after treatment with HKUST-1 and HLV was not significantly reduced when the uranium concentration was very low.

### Table 3: Maximum adsorption capacity of various adsorbents for U(VI) ions

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>pH</th>
<th>(m/V) (g L(^{-1}))</th>
<th>(Q_m) (mg g(^{-1}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified aluminosilica</td>
<td>3.5</td>
<td>1.0</td>
<td>83.30</td>
<td>39</td>
</tr>
<tr>
<td>Modified red muds</td>
<td>3.0</td>
<td>3.5</td>
<td>124.56</td>
<td>41</td>
</tr>
<tr>
<td>Br-PADAP-impregnated MWCNTs</td>
<td>6.3</td>
<td>0.1</td>
<td>83.40</td>
<td>42</td>
</tr>
<tr>
<td>MNP@PAO</td>
<td>6.0</td>
<td>0.5</td>
<td>216.45</td>
<td>43</td>
</tr>
<tr>
<td>Polyprrole</td>
<td>5.0</td>
<td>1.0</td>
<td>87.72</td>
<td>44</td>
</tr>
<tr>
<td><em>Pseudomonas monteillii</em></td>
<td>5.0</td>
<td>0.3</td>
<td>267.30</td>
<td>45</td>
</tr>
<tr>
<td>AO-MWCNTs</td>
<td>4.5</td>
<td>0.5</td>
<td>99.86</td>
<td>46</td>
</tr>
<tr>
<td>Tetraphenylimidodiphosphinate</td>
<td>6.0</td>
<td>0.4</td>
<td>787.40</td>
<td>47</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>6.0</td>
<td>0.2</td>
<td>14.58</td>
<td>29</td>
</tr>
<tr>
<td>HKUST-1@H(<em>3)PW(</em>{12})O(_{40})</td>
<td>6.0</td>
<td>0.2</td>
<td>430.98</td>
<td>30</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>4.0</td>
<td>0.25</td>
<td>424.88</td>
<td>This work</td>
</tr>
<tr>
<td>HLV</td>
<td>4.0</td>
<td>0.25</td>
<td>424.88</td>
<td>This work</td>
</tr>
</tbody>
</table>

### Fig. 7: Column chart of the adsorption efficiency of HKUST-1 and HLV for real uranium-bearing nuclear waste effluents. pH = 4.0, \(C_{(U)}\)\(_{\text{initial}}\) = 0.3–3.0 mg L\(^{-1}\), \(m/V\) = 0.25 g L\(^{-1}\), and contact time = 30 min.

4. Conclusions

In this work, HKUST-1 and HLV were synthesized in a facile manner by hydrothermal methods and exhibited high-efficiency adsorption capacity for uranium from aqueous solutions, especially high-level uranium-containing wastewater. The optimal adsorption conditions included a pH of 4.0, 0.25 g L\(^{-1}\) of adsorbent dose and 30 min of contact time when the initial uranium concentration was 10 mg L\(^{-1}\). The effect of co-existing ions (K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Al\(^{3+}\) and Sr\(^{2+}\)) on the uranium removal by HLV was studied. Results showed that some co-existing ions (such as Mg\(^{2+}\) and Ca\(^{2+}\)) had significantly effect on the adsorption efficiency for U(VI) by HLV at pH 4 while some ions (such as Al\(^{3+}\) and Sr\(^{2+}\)) had no effect on the adsorption efficiency for U(VI). The adsorption processes of HKUST-1 and HLV were well described by the Langmuir isotherm model and pseudo-second-order kinetic model. The maximum adsorption capacities of HKUST-1 and HLV were 430.98 and 424.88 mg g\(^{-1}\), respectively, which is much higher than that of other reported adsorbents. Moreover, HKUST-1 and HLV exhibited favorable adsorption performance for real U(VI)-bearing wastewater samples in practical application. Compared with HKUST-1, low-cost HLV is a very promising potential adsorbent for the removal of uranium from aqueous solutions.

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

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### References
