Highly efficient removal of arsenic(III) from aqueous solution by zeolitic imidazolate frameworks with different morphology

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HIGHLIGHTS

• Three ZIFs with different morphologies are synthesized via green methods.
• The three ZIFs exhibited excellent As(III) adsorption capacity of over 100 mg/g.
• Surface area of ZIFs is not the dominated factor for arsenic adsorption.
• Hydroxyl substitution is the main mechanism for arsenic removal.

ARTICLE INFO

Article history:
Received 28 February 2015
Received in revised form 30 May 2015
Accepted 3 June 2015
Available online 10 June 2015

Keywords:
Zeolitic imidazolate frameworks
Sorption
Arsenite
Mechanism

ABSTRACT

In this study, zeolitic imidazolate frameworks (ZIFs) sorbents with three different morphology (cubic ZIFs, leaf-shaped ZIFs and dodecahedral ZIFs) were successfully synthesized in aqueous solution via green methods at room temperature and tested for removal of As(III). The ZIFs are all high crystalline, and with a BET surface area of 958.4, 12.7 and 1151.2 m\textsuperscript{2}/g for cubic ZIFs, leaf-shaped ZIFs and dodecahedral ZIFs, respectively. The experiment revealed that all three adsorbents exhibited excellent adsorption capacities of As(III) despite distinct specific surface area and morphology. The adsorption isotherms of cubic ZIFs, leaf-shaped ZIFs and dodecahedral ZIFs were generally fitted by Langmuir model and the maximum adsorption capacities were 122.6, 108.1, 117.5 mg/g, respectively at pH 8.5. At initial concentration of 200 \( \mu \)g/L, As(III) was rapidly decreased to below 10 \( \mu \)g/L by the three ZIFs in 2 h at a adsorbent dosage of 0.2 g/L. It was found that zinc hydroxyl substitution was the main surface complexation method for As(III) adsorption onto the three ZIFs evidenced by the FTIR and XPS results.

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1. Introduction

Arsenic contamination in groundwater is a serious environmental problem, which has received increasing concentrations in last decades in many areas all over the world due to its high toxicity and mobility. In China, about 19 million people have being exposed to drinking water with an arsenic concentration higher than the maximum contaminant level (10 \( \mu \)g/L) that the World Health Organization has recommended in 2001. In order to remove arsenic from aqueous solutions effectively, significant researches have been explored, such as coagulation, precipitation, ion exchange filtration, and adsorption. In general, adsorption process has been regarded as one of the most important and widely used approach in arsenic removal due to its high removal efficiency, easy operation and low cost [1].

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http://dx.doi.org/10.1016/j.colsurfa.2015.06.009
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Among the available adsorbents for removing arsenic, the iron oxides, ferric hydroxides, activated alumina, and other natural materials have been extensively investigated and widely used [2–6]. However, arsenic in its lower oxidation state [As(III)], is much more toxic and mobile than arsenic in the higher oxidation state [As(V)], and has a very low adsorption affinity on many adsorbents as its neutral molecular species in a large pH range [7]. Thus, in many studies, preoxidation of As(III) to As(V) is a prerequisite for most of adsorbents, which will increase the complexity and cost of the adsorption process. Although many materials have been studied for their ability to remove As(III) from aqueous solution, to the best of our knowledge, only a few metal–organic frameworks (MOFs), consisting of metal ions and organic ligands, have been investigated to adsorb contaminants in water. Zeolitic imidazolate frameworks (ZIFs), formed by imidazole ligands and metal ions, are subgroup of MOFs. In contrast to many MOFs, which are water soluble or thermal unstable, ZIFs (e.g. ZIF-8) owe a high chemical stability, high specific surface area and excellent porosity [8,9]. ZIF-8 particles, consisting of zinc and 2-methylimidazole (2-Hmim), is a prototypical subclass of ZIFs with a sodalite (SOD) topology similar to some aluminosilicate zeolites, where T–O–T bridges (T = Si, Al, P) are replaced by Zn–Im–Zn [10]. Currently, ZIF-8 has been widely investigated in gas separation, hydrogen storage, carbon dioxide capture, organic size selective separation and catalysis [11–13]. And there is also an increasing interest in water treatment [14].

Various reaction conditions in the synthesis of ZIFs can cause various ZIFs morphologies [15]. For example, Pan et al. [16] synthesized ZIF-8 with hexagonal face in aqueous solution in 5 min by consuming excess 2-methyimidazole (2-Hmim). He et al. [17] developed a novel method to produce ZIF-8 with a cubic- at a stoichiometric metal and ligand molar ratio of 1:2 in the presence of ammonium hydroxide. Chen et al. [18] reported a two-dimensional morphologies. XRD analysis was carried out on a diffractometer (AXS, Brucker, Germany) with Cu target (40 kV, 40 mA, λ = 1.54059 Å) from 5° to 60°. Arsenic concentrations were measured by an inductively coupled plasma atomic emission spectroscopy machine (ICP-OES, Optima 7100 DV, Perkin Elmer Co. USA). For the measurement of low arsenic concentration samples, inductive coupled plasma mass spectrometer (ICP-MS, SCIEX ELAN DRCe Norwalk, Perkin Elmer Co. USA) was employed. Surface charges of the samples were conducted on a Malvern Zetasizer 2000 (Malvern, UK).

Samples for FTIR determination were ground with spectral grade KBr in an agate mortar with a fixed amount of sample (1% w/w) in KBr to prepare the pellet. XPS data of the adsorbents were examined by an AXIS Ultra spectrometer (Kratos Analytical, Manchester, UK) with an Al K anode (1486.6 eV photon energy, 0.05 eV photon energy resolution, 300 W). All spent samples for the XRD, SEM, FTIR and XPS analysis were collected after contacting with As(III) solution of 34.9 mg/L for 48 h.

2.4. As(III) adsorption experiment

All of the arsenic adsorption experiments were carried out at 25.0 ± 0.1°C in a temperature controller shaker. The adsorption kinetic tests were performed in a glass beaker, containing 500 mL of 34.9 mg/mL As(III) solution. The pH of the arsenic solution was adjusted to 7.0 with 0.1 M HCl and NaOH before adsorption. After 0.1 g adsorbent was introduced into the glass beaker, the solution pH increased to 8.5 soon. Thus, during the whole adsorption process, the pH was kept at 8.5 using 0.1 M HCl and NaOH. After the solution had been stirred for the preselected time, the solid mass was filtered by 0.45 μm membranes before analysis. In another experiments, the pH value was also measured during the adsorption at the initial pH 7.0.

Adsorption isotherm experiments were conducted in 250 mL shaking flasks containing 100 mL of arsenic solution. The initial arsenic concentration varied from 5 mg/L to 80 mg/L and the pH of solution was adjusted to 7.0 ± 0.1. After 20 mg of ZIFs were added to the arsenic solution, these flasks were shaken for 24 h at 180 rpm. At low concentrations, experiments were conducted in 250 mL beakers containing 100 mL of 200 ppb As(III) solutions. The adsorbent dosages varied from 0.06 g/L to 0.4 g/L. Samples were taken at 2nd, 6th and 24th h and filtered by 0.45 μm membranes for ICP-MS analysis. All the solution pH were maintained at 8.5 ± 0.1 during 24 h adsorption.

2. Materials and methods

2.1. Chemicals and materials

All chemicals used in this study were analytical grade reagent. Zn(NO$_3$)$_2$·6H$_2$O and 2-Hmim were purchased from Sigma–Aldrich. As(III) stock solution was prepared with deionized water using NaAsO$_2$. Stock solutions were then freshly diluted with deionized water to predetermined concentrations prior to adsorption experiments.

2.2. ZIFs synthesis

Cubic ZIFs were synthesized at room temperature following the literature [17]. Typically, 0.594 g of Zn(NO$_3$)$_2$·6H$_2$O (2 mmol) and 0.328 g of 2-Hmim (4 mmol) were dissolved in 3 mL of deionized water and 3.76 g of ammonium hydroxide solution (NH$_3$·H$_2$O, 64 mmol), respectively. The two solutions were then mixed together with a magnetic stirrer in 10 min. Dodecahedral ZIF-8 was synthesized by a slightly modified method reported in the literature [16]. Typically, 0.863 g of Zn(OAc)$_2$ and 11.350 g 2-Hmim were first dissolved in 8 mL and 80 mL deionized water, respectively. The two solutions were then mixed under stirring at room temperature for 8 h. Leaf-shaped ZIFs was synthesized following the literature [18]. 0.59 g of Zn(NO$_3$)$_2$·6H$_2$O and 1.30 g of 2-Hmim were dissolved in 40 mL deionized water, respectively. And then the two solutions were mixed under magnetic stirring for 4 h.

All the products were collected by centrifugation and washed with deionized water three times. The obtained materials were dried in an oven at 60°C for 24 h and then kept in a desiccator for use.

2.3. Analytical methods

Nitrogen adsorption–desorption data were collected to measure the surface area and pore size distributions of the three ZIFs by a Micrometrics gas adsorption analyzer (ASAP 2020HD88, Micromeritics, USA). Field scanning electron microscope (FE-SEM) (SU-8020, Hitachi, Japan) was used to characterize the surface morphologies. XRD analysis was carried out on a diffractometer (AXS, Brucker, Germany) with Cu target (40 kV, 40 mA, λ = 1.54059 Å) from 5° to 60°. Arsenic concentrations were measured by an inductively coupled plasma atomic emission spectroscopy machine (ICP-OES, Optima 7100 DV, Perkin Elmer Co. USA). For the measurement of low arsenic concentration samples, inductive coupled plasma mass spectrometer (ICP-MS, SCIEX ELAN DRCe Norwalk, Perkin Elmer Co. USA) was employed. Surface charges of the samples were conducted on a Malvern Zetasizer 2000 (Malvern, UK).

Adsorption isotherm experiments were conducted in 250 mL shaking flasks containing 100 mL of arsenic solution. The initial arsenic concentration varied from 5 mg/L to 80 mg/L and the pH of solution was adjusted to 7.0 ± 0.1. After 20 mg of ZIFs were added to the arsenic solution, these flasks were shaken for 24 h at 180 rpm. At low concentrations, experiments were conducted in 250 mL beakers containing 100 mL of 200 ppb As(III) solutions. The adsorbent dosages varied from 0.06 g/L to 0.4 g/L. Samples were taken at 2nd, 6th and 24th h and filtered by 0.45 μm membranes for ICP-MS analysis. All the solution pH were maintained at 8.5 ± 0.1 during 24 h adsorption.
The effect of pH was conducted at 100 mL of 30 mg/L As(III) solutions, and the pH was adjusted to 7.0, 8.0, 9.0, 10.0, 11.0 during the adsorption. The effect of anions was tested at 100 mL of 20 mg/L As(III) concentrations containing 1 mM/10 mM Na₂SO₄, Na₂HPO₄, Na₂CO₃ and NaCl, and the pH were fixed at 8.5 during adsorption. All the experiments were used 20 mg dodecahedral ZIFs. Besides, 200 mg dodecahedral ZIFs was dispersed into 100 mL of 10 mg/L As(III) solutions for 2 h. The adsorbents were then collected by filtration and regenerated in 0.4 mM NaOH aqueous solutions for another 2 h. At last, the adsorbent was filtered and dried at 120 °C for latter use. The regeneration cycles were repeated for three times and removal rate were calculated.

3. Results and discussions

3.1. Characterization of ZIFs

Fig. 1a–c show the SEM images of the three ZIFs and the physical characteristics are summarized in Table 1. The images clearly reveal that the different 2-Hmim/Zn molar ratios have significant impact on the morphologies of ZIFs. As shown in Fig. 1a, ZIFs synthesized at a 2-Hmim/Zn molar ratio of 2 in the presence of ammonium hydroxide are cubic particles with a uniform size. Ammonium as deprotonated agent is also essential for the crystal formation of cubic ZIFs and drastically reduce synthesis time [17]. Leaf-shaped ZIFs are obtained at the 2-Hmim/Zn molar ratio of 8, which is the key factor to fabricate the unique structure. Leaf shaped ZIFs have quite large size of several microns, but are only 150 nm in thickness. When the Hmim/Zn molar ratio increases to 35, dodecahedral ZIFs particles with a mean size of 0.4 μm are formed.

N₂ adsorption–desorption isotherms of the three ZIFs were investigated to analyze the pore structure and specific surface area. As shown in Fig 1d, both cubic ZIFs and dodecahedral ZIFs are type I isotherm with high N₂ adsorption quantities at low pressure due to the microspore structures with a volume of 0.51 and 0.58 cm³/g, respectively. The slight increase at high pressure may be responsible for the textural macrospores by crystal packing [14]. By contrast, leaf-shaped ZIFs show very low N₂ adsorption quantities and poor pore structure, which might result from the bigger size and higher density. The BET surface area of the three synthesized ZIFs, cubic, leaf-shaped and dodecahedral ZIFs are of 958.4, 12.7 and 1151.2 m²/g, respectively.

Fig. 2. As(III) adsorption (a) kinetics (initial arsenic concentration = 35.4 mg/L) and (b) isotherms (initial arsenic concentration = 5–70 mg/L) of the three ZIFs. Shaking speed = 180 rpm, temperature = 25 ± 0.5 °C. Note, solid line, Langmuir fitting curve, dotted line, Freundlich fitting curve.
Table 1
Structure characteristics of the three ZIFs.

<table>
<thead>
<tr>
<th>Species</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>Pore Volume (cm$^3$/g)</th>
<th>Mean pore size (nm)</th>
<th>Mean particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic ZIFs</td>
<td>958.4</td>
<td>0.51</td>
<td>0.8-1.5</td>
<td>700</td>
</tr>
<tr>
<td>Leaf shaped ZIFs</td>
<td>12.7</td>
<td>0.04</td>
<td>15-17</td>
<td>5000</td>
</tr>
<tr>
<td>Dodecahedral ZIFs</td>
<td>1151.2</td>
<td>0.58</td>
<td>0.7-1.6</td>
<td>400</td>
</tr>
</tbody>
</table>

3.2. Adsorption experiments

As(III) adsorption kinetics of the three ZIFs are shown in Fig. 2a. The adsorption equilibrium for all ZIFs reached within 10 h and almost 95% of As(III) are removed from the aqueous solution. Compared with other two ZIFs, the leaf-shaped ZIFs show faster adsorption in the initial stage, which may be attributed to the higher point of zero charge ($pH_{\text{pzc}}$) than the other two ZIFs as shown in Fig 3d. The higher $pH_{\text{pzc}}$ of the particles enables to generate the stronger electro interaction between them.

The adsorption isotherms were also investigated to measure the adsorption capacities and behaviors of As(III) on the three ZIFs as shown in Fig. 2b and the comparison between ZIFs and other adsorbents are summarized in Table 2. The Langmuir isotherm model better fits the experimental data than Freundlich model with a higher $R^2$ as shown in Table 1, indicating that monolayer adsorption may happen to As(III) adsorption. Table 1 also summarizes the maximum adsorption capacities ($Q_m$) of As(III) on the three ZIFs, which are 122.6, 108.1, 117.5 mg/g, respectively. As shown in Table 3, traditional carbon and zeolites have poor adsorption ability on arsenic removal, especially for As(III). While, our work shows that the ZIFs perform considerable adsorption in term of As(III) removal. It is worthwhile to figure out that higher specific surface area usually benefits to more active sites for adsorption, leading to higher capacities [1]. While in this study, the adsorption capacities of the three ZIFs are quite similar in spite of a significant difference between the specific surface areas of the three ZIFs. Typically, for leaf-shaped ZIFs, although its specific surface area is only 1% of those of the other two ZIFs, its adsorption capacity of As(III) is only slightly lower than the other two ZIFs. The results clearly show that surface area is not the dominated factor in the adsorption of As(III) on ZIFs.

The adsorption performances of the three ZIFs at low concentration As(III) are illustrated in Fig. 3a-c. All the three ZIFs can remove As(III) at low concentration efficiently in a sorbent dosage of 0.2 g/L. As(III) concentration in the solution decreases to below 10 μg/L from the initial concentration of 200 μg/L after 2 h of adsorption. This indicates that ZIFs may have a promising application on the drinking water treatment. In addition, further increasing the dosage of the ZIFs can slightly increase the removal rate of As(III). It is worth noting that the concentrations of residual As(III) in the solution on cubic ZIFs and leaf-shaped ZIFs increase at the extended adsorption time, 6 and 24 h. It means that desorp-
tion happened to the two ZIFs so that they may be only suitable for a quick adsorption of As(III). By contrast, even though there is a slight increase of the concentration of residual As(III) after 24 h for dodecahedral ZIFs, desorption is inhibited when the adsorbent dosage reaches 0.4 g/L, showing that dodecahedral ZIF is a much more stable than the other two ZIFs.

3.3. As(III) adsorption mechanism

3.3.1. XRD analysis

Fig. 4 displays the XRD pattern of the three ZIFs before and after adsorption. Fresh cubic ZIFs and dodecahedral ZIFs have similar XRD patterns, indicating the same lattice structures of the two ZIFs, which is consistent with the literatures [16,17]. On the contrary, leaf-shaped ZIFs have different lattice structures. This could be the reason that its surface area is extremely low. However, the spent cubic ZIFs and leaf-shaped ZIFs show the similar XRD patterns after the adsorption of As(III). Most of the original peaks of the fresh ZIFs disappeared, while two new peaks emerged at 12° and 24°, indicating that re-structuring of the two ZIFs happen during the adsorption process. The new peaks at 12° and 24° also appear in the pattern of spent dodecahedral ZIFs, suggesting similar re-structuring happened to dodecahedral ZIFs. Meanwhile, most of the original peaks of fresh dodecahedral ZIFs can still be observed although their intensities dramatically decrease, which means that the structure of the dodecahedral ZIFs particles is retained at some extent.

The spent ZIFs after adsorption were characterized by SEM to study the changes in their morphologies. As shown in Fig. 5a, after adsorption, the cubic ZIFs particles turn into irregular micro-size sheets and few cubic particles are observed. The uniform leaf-shaped ZIFs also turn to similar irregular sheets. The changes in morphologies are in great agreement with the variations of the XRD patterns. However, a small fraction of dodecahedral particles still remain their structures after adsorption of As(III) as shown in Fig. 5c and d, while the majority have transformed to irregular sheets as well. This confirms that the re-structuring of dodecahedral ZIFs is slower than the other two ZIFs.

3.3.2. FT-IR analysis

Fig. 6a and b present the variations of FTIR spectra of the three ZIFs before and after adsorption. It is plain to see that the three ZIFs have similar FTIR spectra before adsorption. This might be explained by that the same assembling forces between imidazole molecules and zinc atoms in the three ZIFs. Generally, the wide band around 3000 cm⁻¹ is the vibration of the intermolecular hydrogen bonding of OH and NH groups of 2-Hmim [11,26]. In addition, some characteristic peaks, for example, 421 cm⁻¹ (Zn–N) and 1580 cm⁻¹ (stretching vibration of C=N), 1380 cm⁻¹ (–CH₃ bending) can also be observed. The peaks at 1350–1500 cm⁻¹ can be assigned to the stretching of the ring of the 2-methylimidazole. The peaks at 900–1350 cm⁻¹ are contributed to the in-plane vibration of ZIFs while peaks at around 800 cm⁻¹ are assigned to the out-plane bending [27].

As shown in Fig 6a, after As(III) adsorption, the wide band near 3000 cm⁻¹ of the three ZIFs shift to higher frequency (3300 cm⁻¹), indicating new bonding of the OH groups with higher energy are formed [29]. In addition, in-plane and out-plane bending of the imidazole ring disappear for cubic ZIFs and leaf-shaped ZIFs while the intensity dramatically decreases for dodecahedral ZIFs (Fig. 6b). At the same time, no obvious change is observed for the absorbance at 750 cm⁻¹ which is assigned to the vibration of –CH groups of the imidazole molecules, indicating the existence of ligands. The peaks at 870 cm⁻¹ might be the complex of As–O [30]. The formation of new protonated N–H groups (1650 cm⁻¹) and the decrease of Zn–N (421 cm⁻¹) manifest the bonds breaking between zinc and 2-methylimidazole. The new peaks with increasing intensity at 460, 510, 540 and 460 cm⁻¹ can be ascribed to the vibration of metal oxygen bonds and the peaks at 1050 cm⁻¹ might be the vibration of Zn–OH. All of these showed an formation amount of Zn–OH [28]. Thus, the Zn–OH could be supplied during the adsorption, causing an considerable adsorption capacities of As(III). Hence, the substitution of hydroxyl of formed Zn–OH might be the main mechanism for As(III) adsorptive removal by ZIFs, which is further evidenced by that the blue shifts of –OH at 3000 cm⁻¹ [31].

3.3.3. XPS analysis

The XPS analysis was conducted on the three ZIFs before and after adsorption of the As(III) to further illustrate the adsorption mechanism. As shown in Table 4, the core level binding energy for arsenic remained at 44.1 to 44.3 eV after adsorption. This shows that no oxidation or reduction reaction occurred during the adsorption [4]. The binding energies at 1021.5 eV and 1044.4 eV for Zn₂p shown in Fig. 7a are ascribed to Zn₂p3/2 and Zn₂p1/2, respectively. After loaded with As(III), the peak for Zn₂p shifts to higher binding energy, implying an interaction with the arsenic species.

Table 2

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>pH</th>
<th>Adsorption capacities (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecahedral ZIFs</td>
<td>8.5</td>
<td>117.5</td>
<td>This work</td>
</tr>
<tr>
<td>Coal based AC</td>
<td>6.0</td>
<td>1.49</td>
<td>Ref. [21]</td>
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<tr>
<td>MIO–CNT</td>
<td>7.0</td>
<td>24.05</td>
<td>Ref. [22]</td>
</tr>
<tr>
<td>nZVI–AC</td>
<td>6.5</td>
<td>18.20</td>
<td>Ref. [23]</td>
</tr>
<tr>
<td>Fe–eZ</td>
<td>7.0</td>
<td>0.10</td>
<td>Ref. [24]</td>
</tr>
<tr>
<td>Fe/Al–Z</td>
<td>5.0</td>
<td>3.86</td>
<td>Ref. [25]</td>
</tr>
</tbody>
</table>

Note: AC: active carbon, MIO–CNT: magnetic iron oxide/carbon nanotube, nZVI: nano-zerovalent iron, Fe–eZ: iron exchanged zeolite, Fe/Al–Z: zeolite supported by bimetallic(Fe/Al) oxide.

Table 3

Comparison between As(III) adsorption capacities for ZIFs and other zeolites and carbon-based adsorbents.

<table>
<thead>
<tr>
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<td>Fe/Al–Z</td>
<td>5.0</td>
<td>3.86</td>
<td>Ref. [25]</td>
</tr>
</tbody>
</table>

Fig. 4. XRD patterns of the comparison of the ZIFs before/after adsorption and after desorption.

Fig. 6a. XRD patterns of the comparison of the ZIFs before/after adsorption and after desorption.
The O1s spectra of each oxide can be divided into the hydroxyl groups interacted with the unsaturated zinc (OH, 531.10 eV) and sorbed water molecules (H2O, 532.00 eV) [32]. As shown in Fig 7(b–d), before adsorption, the sorbed water and Zn—OH has a very low intensity in XPS spectra, indicating low content of oxygen in fresh ZIFs. After As(III) adsorption, the intensity of these oxygen species increase markedly while the nitrogen decreased, demonstrating a considerable amount of Zn—OH might be formatted, furtherly manifesting the Zn—N deformation and Zn—OH formation. Moreover, the core binding energies of OH group decrease, indicating an interaction with the arsenic species [Zn—O—As] [33]. In our previous study, it was also found that OH groups could be substituted by the arsenic species, and increased the electro density of oxygen atoms, resulting in lower core binding energies [34]. Similarly, Wu and Li’s work also found that the Zn—OH is responsible for the adsorptive removal of As(V). Consequently, the OH group became the main species on the three ZIFs after arsenic adsorption and could be formatted during the adsorption [35,36].

Based on the FTIR and XPS analysis, adsorption mechanism of As(III) on ZIFs is proposed as illustrated in Fig. 8. The water molecules are first adsorbed on the unsaturated zinc atoms on the surface of the ZIFs, generating a small quantity of Zn—OH groups. After interacting with the As(III) in aqueous solution, the water and As(III) molecules affect the equilibrium of the Zn—N, resulting the breaking of Zn—N partially (shown in Fig. 8b). Thus, the Zn—OH might be provided from the breaking Zn—N groups continuously, leading to an abundant Zn—OH source on the surface and limited changes on adsorption ability arisen by morphology and surface area. The resultant Zn—OH groups in turn adsorb the arsenic species through OH substitution and form a new bond, Zn—O—As, on the surface. The Zn—O—As is the main interaction way for the adsorption of As(III) on ZIFs, which is be evidenced by the FTIR and XPS
spectra. During the adsorption, the morphology and structure of the ZIFs would turn into layers due to the partial breaking of Zn—N.

3.4. Adsorption properties of dodecahedral ZIFs

According to the mentioned above, the three ZIFs share the same mechanism and the dodecahedral ZIFs was found to be the most suitable ZIFs for As(III) removal in aqueous solution for its considerable stability. Thus the conditional adsorption properties of As(III) adsorption on dodecahedral ZIFs was investigated. Fig. 9a illustrate the pH evolution during the adsorption. Obviously, the solution pH rapidly increased to 8.0 in 5 min and reached equilibrium at 8.5 in 5 h, which is similar to the adsorption kinetics.

The effect of pH on As(III) adsorption capacities (Qe) on dodecahedral ZIFs is summarized in Fig. 9b. The Qe was increased from 79.2 to 109.8 mg/g with the pH ranged from 7 to 9, then decreased with the pH increased continuously. That could be explained by the electro interaction between As species and adsorbent’s surface. The As(III) was neutral molecular (H₃AsO₃) when pH below 8 and exert adverse effects on As(III) adsorption. When the pH was

Table 4

<table>
<thead>
<tr>
<th></th>
<th>Zn₂p</th>
<th>O₁s</th>
<th>As₃d</th>
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<tr>
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<td>H₂O</td>
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<td>Cubic ZIFs</td>
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<td>Leaf-shaped ZIFs</td>
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<td></td>
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<td>Dodecahedral ZIFs</td>
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<tr>
<td></td>
<td>1021.95</td>
<td>531.97</td>
<td>531.11</td>
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</table>
higher than 9, the surface charges converted to negative and hindered the adsorption of anions (H$_2$AsO$_3^{2-}$). Thus the adsorption abilities would decrease again.

The effects of competitive anions at different initial concentrations on As(III) adsorption on dodecahedral ZIFs are shown in Fig. 9c. The $Q_e$ was determined to be as low as 11.6 mg/g in the presence of 1 mM phosphate. In addition, the adsorption was also significantly impeded in the presence of carbonate. However, the presence of vast sulfate and chlorine (even increased to 10 mM) did not cause apparent influence on As(III) adsorption, indicating an inner adsorption.

The durability of dodecahedral ZIFs on As(III) adsorption is demonstrated in Fig. 9d. The removal rate still remains 90% after two recycles and but decreased to around 80% after the third cycle. This might be caused by the leakage of zinc during desorption process, indicating that the durability needs to be improved.

### 4. Conclusion

Three ZIFs, with different morphologies and surface areas, were successfully synthesized through green methods. The ZIFs are all high crystalline, and show great adsorption capabilities to As(III) species, with a maximum adsorption value of 122.6, 108.1, 117.5 mg/g for cubic ZIFs, leaf-shaped ZIFs and dodecahedral ZIFs, respectively. It was found that neither surface area nor morphology was the main factor of the As(III) adsorption based on the kinetics and isotherms. All the ZIFs could remove the As(III) concentration below 10 $\mu$g/L at a dosage of 0.2 g/L. The dodecahedral ZIFs particles, showed highest stability at both high and low As(III) concentration. The FTIR and XPS data indicated that Zn–OH groups, generated from unsaturated zinc and broken Zn–N, are the main sites for arsenic adsorption through OH substitution.

### Acknowledgements

This work was partially supported by the key project of the National “863” High-tech R&D Program of China (2012AA062604). The authors would like to acknowledge the Joint Research Fund for Overseas Chinese Scholars and Scholars in Hong Kong and Macao (51328803) awarded by the National Natural Science Foundation of China.