Superior removal of inorganic and organic arsenic pollutants from water with MIL-88A(Fe) decorated on cotton fibers

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Abstract

Arsenic contamination has attracted worldwide concerns, owing to its toxicity and severe threat to human and environment. It is urgent to develop efficient adsorbents to remove arsenic pollutants. Within this paper, both pristine MIL-88A(Fe) and MIL-88A(Fe) decorated on cotton fibers were successfully fabricated using an eco-friendly method. The pristine MIL-88A(Fe) displayed outstanding adsorption performances towards four selected arsenic pollutants, in which the adsorption capacities toward As(III), As(V), ROX and ASA were 126.5, 164.0, 261.4 and 427.5 mg g⁻¹, respectively. Additionally, MIL-88A(Fe) exhibited excellent removal efficiencies in a wide pH range and with the presence of different co-existing ions. It was proposed that the coordinative interactions of As-O-Fe between arsenic pollutants and MIL-88A(Fe) contributed to the superior adsorption performances. Furthermore, two MIL-88A(Fe)/cotton fibers composites were synthesized by both post synthesis (MC-1) and in-situ synthesis (MC-2), which demonstrated identically outstanding adsorption activities toward four selected arsenic pollutants. MC-1 and MC-2 enhanced the stability and reusability of MIL-88A(Fe), which was challenging issues of pristine MIL-88A(Fe) powder. Additionally, the fixed-bed column packed by MC-1 or MC-2 can continuously eliminate arsenic pollutants from the water flow. This work provided a new possibility of metal-organic frameworks to accomplish potentially large-scale application to purify the arsenic-contaminated water.
1. Introduction

Among toxic elements, arsenic (As) is one of the most hazardous contaminants in water environment, as it is originated from natural sources like soils, rocks along with volcanic activity, and anthropogenic sources like wood preservatives, pesticides, pharmaceuticals, pigment industries (Hughes et al., 2011). The long-term and chronic exposure to arsenic contaminated water can lead to diarrhea, muscle weakness, neurological disorder, irregular heartbeat, impairments of the immune system, cancers, and even death in extreme cases (Hughes et al., 2011; Moghimi et al., 2015; Song et al., 2017). Hence, the maximum permissible arsenic level in drinking water has been set as 10 μg L⁻¹ by the Environmental Protection Agency (EPA) and World Health Organization (WHO) (Smith et al., 2002). Generally, the arsenic mainly exists as inorganic forms of As(V), As(III) and organic compounds like arsanilic acid (ASA, C₇H₆AsNO₃), roxarsone (ROX, C₇H₆AsNO₃) in water environment. Inorganic As(III) are highly toxic, which is approximated 60 times more poisonous than inorganic As(V) (Smedley and Kinniburgh, 2002). Organic arsenic like ASA and ROX are widely used as feed additives in the pork and poultry industries, which can be emitted into water and soil (Sierra-Alvarez et al., 2010; Wang and Cheng, 2015), which can eventually be converted into highly toxic inorganic As(III) and As(V) compounds (Jun et al., 2015). Therefore, the removal of both inorganic and organic arsenic is highly significant and desirable (Wang et al., 2019). So far, many techniques like oxidation, precipitation, coagulation, coprecipitation, sorption, membrane have been adopted to achieve arsenic removal (Ahmad et al., 2020; Choong et al., 2007; Guan et al., 2012; Zhang et al., 2019). Adsorption is regarded as a promising technique due to its low cost, simple operation, no need of expensive reagents and catalysts as well as proceeding at ambient operation temperature/pressure (Jung et al., 2015). Adsorption technology is desirable due to simple operation and low cost, which is strongly dependent on adsorbents. Traditional adsorbents including activated carbon (Chen et al., 2007), metal oxides (Joshi et al., 2017), and polymers (Poon et al., 2014) have been investigated, which are facing some problems like low adsorption capacity, and slow adsorption rate. It is still important and challenging to explore efficient and eco-friendly adsorbents for the superior decontamination of arsenic in water.

Metal-organic frameworks (MOFs), three-dimension frameworks built up of metal templates and organic linkers, are unique types of highly porous crystalline materials (Cai et al., 2016; Wang et al., 2014). Benefiting from the controlled porosity, ultra-high specific surface areas, structural tailorability, MOFs have been extensively investigated in catalysis and photocatalysis (Wang et al., 2019; Yi et al., 2019), adsorption toward inorganic As(III), inorganic As(V), ASA and ROX in batch and continuous experiments, in which the adsorption kinetics, thermodynamics, influence factors and mechanism was investigated. This work provided a new possibility to clean pollutants from water with adsorbents loaded on substrates like natural cottons.

2. Experimental

The used chemicals and reagents along with the corresponding characterization instruments were listed in Electronic Supplementary Information (ESI).

2.1. Synthesis of MIL-88A(Fe)

MIL-88A(Fe) was prepared by using an eco-friendly method (Fu et al., 2020), which was described in ESI.

2.2. Fabrication of MIL-88A(Fe)/Cotton

2.2.1. Post synthetic method

1.0 g pure cotton fabric and 1.0 g as-prepared MIL-88A(Fe) powder were mixed into 150 mL of deionized water, which was agitated by magnetic stirrer for 8 h with a speed of 850 rpm at room temperature. The obtained MIL-88A(Fe)/Cotton (MC-1) was washed with deionized water and ethanol (99%) several times to remove the weakly bonded MIL-88A(Fe), and dried at 333 K until the complete evaporation of water and ethanol, which can guarantee the uniformity of the as-prepared MIL-88A(Fe)/cotton fibers composites. The parallel fabrication experiments were carried out for 10 times to ensure the controlled amount of MIL-88A(Fe) being coated onto cotton fibers, in which the relative errors of loaded amounts of MIL-88A(Fe) onto cotton fibers is within ±5% (Table S1).

2.2.2. In-situ growth method

The procedure for in-situ growth of MIL-88A(Fe)/Cotton (MC-2) was similar to the synthesis of pristine MIL-88A(Fe) (Section 2.1), expect that 1.0 g pure cotton fabric was added to the aqueous solution containing 1.0 mmol FeCl₃·6H₂O (2.7029 g) and 1.0 mmol fumaric acid (1.1607 g). The obtained MC-2 was washed by deionized water and ethanol (99%) several times to remove the unbounded MIL-88A(Fe), and dried at 333 K until the complete evaporation of molecular water and ethanol. The parallel fabrication experiments were carried out for 10 times, which was identical to that of the MIL-88A(Fe)/Cotton (MC-1).

2.3. Adsorption experiments

The adsorption kinetic studies were performed at pH = 5 for
ROX, at pH = 11 for ASA, As(III) and As(V) with the initial inorganic arsenic solution concentration from 1 to 50 mg L\(^{-1}\) along with the initial organic arsenic solution concentration from 1 to 150 mg L\(^{-1}\), while the dosages of the pristine MIL-88A(Fe) as adsorbent were kept at 0.2 g L\(^{-1}\). To obtain the adsorption isotherms and thermodynamic parameters, the corresponding experiments were conducted under 298 K, 303 K and 308 K at a speed of 170 rpm for 48 h.

The experiments towards simulate different treated water samples (the details are listed in Table S2) were performed by adding 0.4 g MIL-88A(Fe), 0.54 g MC-1 or MC-2 to 200 mL inorganic and organic arsenic solution. During the adsorption process, every 4.0 mL samples were drawn with spinge filter (0.22 μm) from the mixtures. The residual inorganic and organic arsenic concentrations were determined by ICP-OES (ICP-5000, Focused Photonics Inc., China) with the detection limit being 5.5 μg L\(^{-1}\).

2.4. Fixed-bed column experiments

The fixed-bed column experiments were performed to investigate the potential large-scale application, in which 1.08 g MC-1 or 1.08 g MC-2 was packed in a glass column with length of 340 mm and diameter of 16 mm. As illustrated in Fig. 12a, the flow rate in term of the superficial liquid velocities (SLV) is maintained as 6.0 mL min\(^{-1}\) by a constant flow longer precision pump. The bed depth, bed volume, empty bed contact time (EBCT) and hydraulic loading rate are listed in Table S3. The simulated wastewater samples containing organic arsenics (like ROX and ASA) with concentration of 10.0 mg L\(^{-1}\) and inorganic arsenics (like As(III) and As(V)) with concentration of 0.5 mg L\(^{-1}\) were pumped through the column from top to bottom. The residual inorganic and organic arsenic concentrations in the effluent were measured by ICP-OES with the detection limit being 5.5 μg L\(^{-1}\).

2.5. Data analysis

The adsorption kinetic were analyzed by the pseudo-first-order and pseudo-second-order kinetic models, Langmuir isotherms, Freundlich and Dubinin–Radushkevich adsorption models were applied to fit the adsorption isotherms. Thermodynamic parameters were obtained by previous reported method. Details of the methods are described in the Supporting information.

3. Results and discussion

3.1. Characterization

The peaks at 7.6°, 10.2°, 13.0°, 14.1°, 15.2° and 20.9° in the powder X-ray diffraction (PXRD) patterns (Fig. S1) of the as-prepared MIL-88A(Fe) matched well with those of the previously reported MIL-88A(Fe) (Liu et al., 2018; Xu et al., 2014), implying that MIL-88A(Fe) could be synthesized adopting our reported method. In the PXRD patterns of MC-1 and MC-2, the peaks at 14.7°, 16.6° and 22.8° were ascribed to the cotton fibers, while the characteristic peaks of MIL-88A(Fe) couldn’t be observed due to the tiny content of MIL-88A(Fe) in the MC-1 and MC-2 samples (Fig. S1) (Abdelhameed et al., 2018). Possibily, the strong diffraction peaks of cotton fibers could overlap the relatively weak diffraction peaks of MIL-88A(Fe), which was similar to the Uio-66-NH\(_2\) decorated on Al\(_2\)O\(_3\) substrate (Du et al., 2019).

Moreover, the FTIR spectra of the as-prepared MIL-88A(Fe), MC-1 and MC-2 samples were depicted in Fig. S2. As to the as-prepared pristine MIL-88A(Fe), the broad absorption band appearing around 3300–3500 cm\(^{-1}\) were ascribed to the O−H stretching vibrations of the water molecules (Gholizadeh Khasevani and Gholami, 2018). The two intense peaks at 1396 cm\(^{-1}\) and 1603 cm\(^{-1}\) were assigned to the symmetric and asymmetric vibration modes of the carboxyl group, respectively, indicating that the dicarboxylate linkers were presented in the MIL-88A(Fe) framework (Gholizadeh Khasevani and Gholami, 2018; Liu et al., 2018). The peaks at 560 cm\(^{-1}\) was ascribed to the Fe−O vibration of MIL-88A(Fe) (Lv et al., 2015). As to the cotton fibers, the peak at 1642 cm\(^{-1}\), 2890 cm\(^{-1}\) and 3327 cm\(^{-1}\) were contributed to the stretching vibration of C−C−, −CH\(_3\) and −OH group, respectively (Gargoubi et al., 2016; Lv et al., 2014). These absorption peaks were corresponding to the structure of cellulose in cotton fibers. The characteristic peaks at 560 cm\(^{-1}\), 1396 cm\(^{-1}\) and 1603 cm\(^{-1}\) in both MC-1 and MC-2 were originated from MIL-88A(Fe) decorated on the cotton fibers, affirming the successful fabrication of MIL-88A(Fe)/cotton. It is noteworthy noting that a new peak at 1724 cm\(^{-1}\) in MIL-88A(Fe)/cotton is attributable to COOH group and COOR group (not carboxylate).

These peaks suggest that esterification reaction took place between the carboxyl group of MIL-88A(Fe) and the hydroxyl group of cotton surface (Fiamingo and Campana-Filho, 2016; Xu et al., 2017). The morphology and particle size of as-prepared MIL-88A(Fe) were investigated by SEM and TEM images. As illustrated in Fig. 1, the pristine MIL-88A(Fe) displayed uniform and well-crystallized hexagonal micro-rods with an average size of 700–1200 nm in length and 200–400 nm in diameter, which was slightly smaller than those in the previous reports (Huang et al., 2018; Liu et al., 2018; Xu et al., 2014). As to MC-1, MIL-88A(Fe) particles were uniformly distributed over cotton fibers (Fig. 2a and b and Fig. S3a). While, as to MC-2, the MIL-88A(Fe) particles were distributed densely (Fig. 2d and Fig. S3b) or sparsely (Fig. 2e) over partial locations of the cotton fibers. The successful decoration of MIL-88A(Fe) on cotton fibers was further affirmed by the elemental mapping (Fig. 2c and f).

To determine the surface composition and chemical states of MC-1 and MC-2, the X-ray photoelectron spectrum (XPS) analysis was conducted. As displayed in Fig. 3a, the characteristic peaks of C, O and Fe were observed in the XPS spectra of MC-1 and MC-2. As found in Fig. 3b, the C 1 s spectrum was divided into four peaks at binding energy of 288.54, 287.02, 286.00 and 284.38 eV in MC-1 and 288.51, 287.29, 286.02 and 284.41 eV in MC-2. The carboxylate groups and C−C of the completely deprotonation of fumarate were corresponded to the peaks with binding energies at 288.54/288.51 eV and 284.38/284.41 eV, respectively (Huang et al., 2018; Liao et al., 2019; Liu et al., 2018). The peaks with binding energy of 286.00/286.02 eV, 287.02/287.29 eV and 288.54/288.51 eV in MC-1 and MC-2 could be ascribed to C−O−C−OH and C−O−C−O of cotton fibers and ester groups (Xu et al., 2017; Yang et al., 2009). Fig. 3c displayed the high-resolution XPS spectra of O 1s, which could be split into five peaks at binding energies of 533.54/533.32 eV, 532.98/532.93 eV, 532.34/532.49 eV, 531.69/531.86 eV and 530.51/530.91 eV, attributing to the O−H of the surface hydroxyl groups, the C−O and O−C=O bond of cotton fabric and ester groups, oxygen components on the carboxylate groups of the fumarate and the Fe−O bonds of the MC-1/MC-2, respectively (Ding et al., 2018; Liao et al., 2019; Liu et al., 2018). These results further affirmed that MIL-88A(Fe) have been covalently linked on cotton surface via formation of ester groups (Naebe et al., 2018). As shown in Fig. 3d, the high-resolution XPS spectrum of Fe 2p could be divided into the Fe 2p\(_{3/2}\) (711.2/711.28 eV) and Fe 2p\(_{1/2}\) (725.01/725.05 eV) with a satellite signal at 715.66/715.27 eV for MC-1 and MC-2. The peak distance between the Fe 2p\(_{3/2}\) and the Fe 2p\(_{1/2}\) was approximately 13.8 eV, which was well coincide with previous references for Fe\(_2\)O\(_3\), which was slightly smaller. Furthermore, the binding energy of Fe 2p doublet for MC-1 and MC-2 displayed the mild shift of binding energy to the lower energy in comparison with the Fe(III) typical peaks of the MIL-88A(Fe).
the compact interfacial contact between MIL-88A(Fe) and cotton fibers in the MC-1 and MC-2 (Liang et al., 2015a,b; Xia et al., 2019). According to previously reported papers (Muniz et al., 2009; Xia et al., 2019), the presence of Fe(III) species facilitated to oxidize more poisonous As(III) into lower toxicity As(V), which was favorable to be adsorbed onto the surface of adsorbents. The loaded MIL-88A(Fe) was slightly high for post synthetic composite (ca. 80.0 mg g\(^{-1}\)) and exceeded the amounts loaded onto the in-situ composite (ca. 60.0 mg g\(^{-1}\)). In all, the XPS determination along with FTIR, PXRD, SEM and TEM confirmed the successful decoration of MIL-88A(Fe) onto cotton fibers.

3.2. Adsorption kinetics

The adsorption rate is a key factor for efficiently treating As-containing water (You et al., 2020; Yu et al., 2019). To gain an insight into the adsorption kinetics behaviors of MIL-88A(Fe), the time-dependence of inorganic and organic arsenic removal with various initial concentrations were given in Fig. S4, Fig. S6, Fig. S8 and Fig. S10. For the initial As(III) concentrations of 1 and 5 mg L\(^{-1}\), when the equilibrium was reached, the As(III) removal efficiency reached 98.12 and 95.60% within 120 min, respectively. For the initial ROX, ASA, As(V) concentrations of 1, 5 and 10 mg L\(^{-1}\), the adsorption equilibrium can be rapidly reached within 30 min, and the residual arsenic concentration could be declined to below 10 \(\mu\)g L\(^{-1}\). Considering that the concentrations of organic and inorganic arsenics in the water environment even in contaminated water body were always low (generally no more than 2.5 mg L\(^{-1}\)), the adsorption behaviors of MIL-88A(Fe) indicated that it was an outstanding and potential adsorbent for highly effective arsenic capture in the practical application. The corresponding fitted kinetic parameters were listed in Table S4, Table S7, Table S10 and Table S13. All the sorption kinetic curves were more fitted in the pseudo-second-order model with the outstanding correlation coefficients \((R^2 > 0.995)\) and the theoretical adsorption capacities calculated from the pseudo-second-order kinetic model were in good agreement with the experimental values (Table S4, Table S7, Table S10 and Table S13). The results demonstrated that the rate-controlling step might be chemisorption, and the adsorption capacity were determined by the number of active sites (B. Liu et al., 2015).

3.3. Adsorption isotherms

In order to determine the maximum adsorption capacity and adsorption isotherms behaviors of MIL-88A(Fe), the adsorption isotherm studies were conducted. The adsorption isotherms behaviors of MIL-88A(Fe) at different temperatures like 298, 303 and 308 K toward different organic and inorganic arsenic with different initial concentrations were presented in Fig. S5, Fig. S7, Fig. S9 and Fig. S11, respectively. The maximum adsorption capacity of pristine MIL-88A(Fe) towards As(III), As(V), ROX and ASA was 126.5, 164.0, 261.4 and 427.5 mg g\(^{-1}\), respectively, which was higher than those of counterpart adsorbents listed in Table 1. Although some adsorbents like the UiO-66, UiO-67 and ZIF-8 (Wang et al., 2019) could achieve higher adsorption capacity toward selected arsenic pollutants than MIL-88A(Fe), it was worthy noting that the as-
prepared MIL-88A(Fe) displayed superior adsorption performance toward different arsenic pollutants like not only inorganic arsenic pollutants but also organic arsenic pollutants with low concentration. For example, mesoporous ZIF-8 possessed the higher maximum adsorption capacity (791 mg g\textsuperscript{-1}) toward ASA than the as-prepared MIL-88A(Fe) in this study, but the adsorption capacity of MIL-88A(Fe) (q\textsubscript{e,0.03} = 50 mg g\textsuperscript{-1}) was higher than that of mesoporous ZIF-8 (q\textsubscript{e,0.03} = 0.76 mg g\textsuperscript{-1}) toward ASA with equilibrium concentration of 30 \textmu g L\textsuperscript{-1} (Jung et al., 2015). With the good adsorption performance toward different organic and inorganic arsenics, MIL-88A(Fe) could be potentially applied in the treatment of natural wastewater with low contents of arsenic pollutants.

To get further insight into the adsorption isotherms behaviors of MIL-88A(Fe), the adsorption isotherm models, and thermodynamic parameters were studied. As shown in Table S5, Table S8, Table S11 and Table S14, the higher correlation coefficient values and the maximum adsorption capacities calculated from Langmuir plots indicated these adsorption isotherms were well followed the Langmuir model (Wang et al., 2020). All the calculated thermodynamic parameters including the standard free energy \( \Delta G^\circ \), enthalpy \( \Delta H^\circ \) and entropy \( \Delta S^\circ \) were illustrated in Table S6, Table S9, Table S12 and Table S15, respectively. The negative values of all \( \Delta G^\circ \) implied that the adsorption process was spontaneous in the nature. The negative value of \( \Delta H^\circ \) was observed for the adsorptive interaction between MIL-88A(Fe) and ROX indicated the endothermic nature of sorption process, while the positive value of \( \Delta H^\circ \) for the interactions between MIL-88A(Fe) and As(III)/As(V)/ASA revealed that the corresponding processes were exothermic. The positive

Fig. 2. SEM image of (a, b) MC-1 and (d, e) MC-2; Elemental mappings of (c) MC-1 and (f) MC-2.
Fig. 3. XPS spectrums of MC-1 and MC-2: (a) survey spectrum, (b) C 1s, (c) O 1s, and (d) Fe 2p.

Table 1
Comparison of MIL-88A(Fe) with various adsorbents for arsenic removal (298 K).

<table>
<thead>
<tr>
<th>Arsenic species</th>
<th>Adsorbents</th>
<th>Adsorption capacity (mg g⁻¹)</th>
<th>pH</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(V)</td>
<td>MIL-53(Fe)</td>
<td>21.3</td>
<td>5</td>
<td>Vu et al. (2015)</td>
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<tr>
<td>As(V)</td>
<td>Celluω-HPEI fibers</td>
<td>99.3</td>
<td>4</td>
<td>Deng et al. (2016)</td>
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<td>As(V)</td>
<td>Hierarchical ZIF-8</td>
<td>90.9</td>
<td>N/A</td>
<td>Wu et al. (2014)</td>
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<td>As(V)</td>
<td>MIL-100(Fe)</td>
<td>110.0</td>
<td>7</td>
<td>Cai et al. (2016)</td>
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<td>As(V)</td>
<td>NH2-MIL-88(Fe)</td>
<td>125.0</td>
<td>6</td>
<td>Xie et al. (2017)</td>
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<tr>
<td>As(V)</td>
<td>MIL-88B(Fe)</td>
<td>156.7</td>
<td>6</td>
<td>Hou et al. (2018)</td>
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<td>As(V)</td>
<td>MnFeO₃ Magnetic Nanoparticles</td>
<td>68.3</td>
<td>2.1</td>
<td>Hu et al. (2017)</td>
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<td>As(V)</td>
<td>Fe₂O₃@MIL101(Cr)</td>
<td>80.0</td>
<td>7</td>
<td>Folens et al. (2016)</td>
</tr>
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<td>As(V)</td>
<td>MIL-88A(Fe)</td>
<td>164.0</td>
<td>11</td>
<td>This work</td>
</tr>
<tr>
<td>As(III)</td>
<td>CuO nanoparticles</td>
<td>26.9</td>
<td>8</td>
<td>Martinson and Reddy (2009)</td>
</tr>
<tr>
<td>As(III)</td>
<td>Fe₂O₃@ZIF-8</td>
<td>100.0</td>
<td>8</td>
<td>Huo et al. (2018)</td>
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<tr>
<td>As(III)</td>
<td>Fe₂O₃@MIL101(Cr)</td>
<td>121.5</td>
<td>7</td>
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<td>As(III)</td>
<td>2D ZIF-L</td>
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<td>10</td>
<td>Nasir et al. (2018)</td>
</tr>
<tr>
<td>As(III)</td>
<td>MIL-88A(Fe)</td>
<td>126.5</td>
<td>11</td>
<td>This work</td>
</tr>
<tr>
<td>ASA</td>
<td>MnFeO₃ Magnetic Nanoparticles</td>
<td>59.5</td>
<td>2.1</td>
<td>Hu et al. (2017)</td>
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<td>ASA</td>
<td>UiO-67-NH₂</td>
<td>178.0</td>
<td>4</td>
<td>Tian et al. (2018)</td>
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<td>ASA</td>
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<td>238.0</td>
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<td>ASA</td>
<td>MIL-100(Fe)</td>
<td>366.0</td>
<td>4</td>
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<td>ASA</td>
<td>NH₂-MIL-68(In)</td>
<td>401.6</td>
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<td>ASA</td>
<td>MIL-88A(Fe)</td>
<td>427.5</td>
<td>11</td>
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<td>ROX</td>
<td>MnFeO₃ Magnetic Nanoparticles</td>
<td>51.5</td>
<td>2.1</td>
<td>Hu et al. (2017)</td>
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<td>ROX</td>
<td>CNT/GPFe/chitosan</td>
<td>142.9</td>
<td>6</td>
<td>Ma et al. (2015)</td>
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<tr>
<td>ROX</td>
<td>MIL-100(Fe)</td>
<td>387.0</td>
<td>N/A</td>
<td>Jun et al., 2015</td>
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<td>ROX</td>
<td>MIL-88A(Fe)</td>
<td>261.4</td>
<td>5</td>
<td>This work</td>
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</table>
value of $\Delta S$ suggested the increased of randomness during the adsorption process of MIL-88A(Fe) toward different selected arsenic targets (Hu et al., 2017). These results demonstrated that the adsorption of MIL-88A(Fe) toward ROX was a spontaneous, endothermic and the random process, while the adsorptive interactions of MIL-88A(Fe) toward As(III), As(V) and ASA were spontaneous, exothermic and the random processes.

3.4. Effect of pH

The pH value of arsenic solution have a great effect on adsorption characteristics, because it determines surface properties of adsorbents along with the anionic species of arsenic (Nasir et al., 2018). The zeta potentials of as-prepared pristine MIL-88A(Fe) in the pH range of 4.0–12.0 were displayed in Fig. S12, in which it decreased with the increase of pH, and the isoelectric point (IEP) value was ca. 7.0. The adsorption performances of MIL-88A(Fe) towards different organic and inorganic arsenics in the pH range from 2.0 to 12.0 were illustrated in Fig. 4. As to ROX and As(V), efficient removal (nearly 100%) was accomplished at wide pH range from 3.0 to 11.0, and the optimum pH values for ROX and As(V) removal were 5.0 and 11.0, respectively. For ASA, the optimum removal efficiency with maximum value of 94.7% occurred at pH = 11.0, and the removal efficiency of ASA was still maintained over 75% in the pH range of 5.0–10.0. The As(III) removal efficiencies were extremely low under the acidic and weak alkaline conditions (pH ranging from 2.0 to 8.0), and increased rapidly with the increasing pH from 8.0 to 11.0. MIL-88A(Fe) exhibited optimum removal efficiency with 92.6% at pH = 11.0. As well known, the pH values of the treated water samples were controlled in the suitable range, MIL-88A(Fe) also accomplish satisfied As(III) and ASA removal.

3.5. Effect of co-existing ions

As typical trace contaminants, the concentrations of different arsenics in common water environment were reported to be below 2.5 mg L$^{-1}$ and even below 0.5 mg L$^{-1}$ in most cases (Choonng et al., 2007; X. Liu et al., 2015). To test the influences from co-existing ions, tap water, lake water and rain water were adopted to simulate different treated water samples containing selected inorganic arsenics (the concentration of As(III) and As(V): 0.5 mg L$^{-1}$) and organic arsenics (ROX and ASA: 1 mg L$^{-1}$). As illustrated in Fig. 5, the ASA, ROX, As(V) and As(III) concentration decreases dramatically with the addition of MIL-88A(Fe), in which the nearly 100% removal efficiencies could be accomplished within 20, 20, 5, 90 min, respectively. It was worthy to noting that the residual ASA,
ROX, As(V) and As(III) concentrations after being adsorbed by MIL-88A(Fe) were lower than those required by drinking water standards, WHO (10 µg L⁻¹ for As(V), 35 µg L⁻¹ for As(III), 29 µg L⁻¹ for ROX and 35 µg L⁻¹ for ASA) (Choong et al., 2007; Wang et al., 2019). It is noteworthy that the dissolved organic matter (DOM) can strongly interact with inorganic and organic contaminants to affect their transformation, transportation and toxicity (Zhao et al., 2018). In this study, the results revealed that DOM didn’t exert remarkable influence the adsorptive performances of MIL-88A(Fe) towards arsenic contaminants, which was comparable to the adsorptive performances of UiO-67 towards organic arsenic (Tian et al., 2018). Both high removal efficiency and fast equilibrium time suggested that the MIL-88A(Fe) was a highly efficient adsorbent for removing inorganic and organic arsenic pollutants from real water environment.

3.6. Possible adsorption mechanism

Previous researches had verified that the surface area was a significant factor for the adsorption performance (Li et al., 2016). But in this study, the BET surface area of pristine MIL-88A(Fe) is 13.29 m² g⁻¹, implying that its outstanding adsorption performance towards inorganic and organic arsenic might not be assigned to its porous structure (Xiao et al., 2015). The zeta potentials of MIL-88A(Fe) ranged from 1.8 to —6.9 mV at pH being 4.0—12.0, demonstrating that the strong affinity with different arsenic species might not be attributed to electrostatic interaction (Sarker et al., 2017). To further elucidate the interaction between various arsenic pollutants and pristine MIL-88, the elemental mappings, FTIR and XPS spectra of MIL-88A(Fe) were obtained before and after arsenic adsorption. The elemental mapping obtained from SEM verified that the presence of arsenic in MIL-88A(Fe) after adsorbing different arsenics (Fig. 6). The immobilization of arsenic on the surface of MIL-88A(Fe) can be also confirmed by XPS determination (Fig. S13). After adsorbing arsenic, a new binding energy peak appeared at ca. 45.3 eV, which can be ascribed to As 3d peak. Two new peaks with weak intensity at 828 cm⁻¹ and 733 cm⁻¹ appeared in the FTIR spectra of MIL-88A(Fe) adsorbing arsenic adsorption, which corresponded to the protonated As—O(Fe) bond of the adsorbed arsenate and As—O bond in the As—O—Fe linkage (Lv et al., 2015; Sui et al., 2016). The above-stated characterizations confirmed the interactions between arsenics and MIL-88A(Fe).

To further determine the strong affinity between arsenic and MIL-88A(Fe), the high-resolution XPS determinations of O1s in MIL-88A(Fe) before and after arsenic adsorption were conducted. Prior to adsorption, O1s spectra in the pristine MIL-88A(Fe) could be divided into three peaks at 533.5, 531.9 and 530.5 eV (Fig. 7b), corresponding to the surface hydroxyl groups, the oxygen components of the carboxyl groups and the Fe—O bonds in MIL-88A(Fe) (Liang et al., 2015a,b; Xie et al., 2017). After the adsorption toward ROX, a new O 1s peak appeared at 531.34 eV, which could be ascribed to As—O (Kang et al., 2013). The results matched well with the corresponding FTIR spectra analysis. Similar XPS analyses for...
adsorptive interaction between MIL-88A(Fe) and As(III)/As(V)/ASA were performed, and the corresponding XPS and FTIR spectra were illustrated in Fig. S13 and Fig. S14. It was observed that the binding energy of Fe 2p displayed mild deviation to higher energy (Fig. 7c), which can be assigned to the strong interaction between As in ROX and Fe3-μ3-oxo clusters in MIL-88A(Fe) (Hou et al., 2018; Xie et al., 2017). These results indicated that the adsorption of MIL-88A(Fe) toward different arsenic pollutants resulted from the formation of As–O–Fe linkages, which was consistent with the pseudo-second-order adsorption kinetics modeling (Hou et al., 2018) (see Fig. 8).

Furthermore, FTIR, XRD (Fig. S15) and SEM (Fig. S16 and Fig. S17) revealed that the morphology and crystalline structure of MIL-88A(Fe) were well maintained after the interaction with different arsenic species, implying good stability of MIL-88A(Fe) during the adsorption process in water surrounding (Jian et al., 2015).

3.7. The adsorption performances of MC-1 and MC-2

It was well known that it was difficult to achieve recovery and separation of the powder adsorbents (Valizadeh et al., 2018). Our experiment result illustrated in Fig. 11a confirmed that powder MIL-88A(Fe) was hard to be separated from the treated water samples for reuse, as the powder MIL-88A(Fe) was declined to be suspended in the water solution. To solve the awkward situation faced by the powder adsorbents, it was expected to fabricate the adsorbents on some substrates (Du et al., 2019; Li et al., 2019). One of our strategies is to decorate MIL-88A(Fe) on the cotton fibers via both post synthetic method and in-situ growth method. To eliminate possible interference, the controlled experiments were conducted and the results revealed that blank cotton displayed nearly no adsorption activities towards different arsenic species. As depicted in Fig. 9 and Fig. 10, MC-1 and MC-2 exhibited outstanding adsorption activities toward four selected arsenic pollutants in different water samples simulated by pure water, tap water, lake water and rain water. The adsorption rates over MC-1 and MC-2 toward different arsenic pollutants were slower than those of pristine MIL-88A(Fe) (Figs. 9 and 10). As demonstrated in Fig. 11d, the leaking of Iron (Fe) from MC-1 and MC-2 ranged from 0.015 mg L\(^{-1}\) to 0.033 mg L\(^{-1}\) during the adsorption process, which were much lower than the pristine MIL-88A(Fe). Furthermore, the residual arsenic solution after adsorptive treatment using MC-1 and MC-2 were clear (Fig. 11b and c), which exhibited good recovery and separation superior to MIL-88A(Fe) powder (Fig. 11a). The results demonstrated that MIL-88A(Fe)/cotton fibers exhibited excellent removal efficiency and fast equilibrium rate towards different arsenic pollutants. Due to ultrahigh adsorption capacity, MIL-88A(Fe)/cotton fiber composites can be used for many times in simulated nature water until reaching adsorptive saturation. Furthermore, MIL-88A(Fe) was hard to be separated from the surface of cotton fibers during adsorption process and nearly no substance leaked to the water environment. The cotton fibers can be processed into thread and further be weaved into mesh, which can be put into treated water to capture arsenic pollutants and be pulled from the water after adsorptive saturation.

3.8. Fixed bed column experiments

The continuous adsorptive removal toward pollutants in fixed-bed column is always desired in large-scale operation due to that it is easy to operate and offers us many useful parameters during pollutants removal (Wang et al., 2015). In this study, the column was packed by MIL-88A(Fe)/cotton fibers rather than the individual MIL-88A(Fe) particles to avoid the loss of packed adsorbent particles and to guarantee the rapid flow of targeted solution. The fixed bed column was adopted to remove the inorganic and organic arsenic pollutants from continuous flow of simulated wastewater (Fig. 12a), in which the concentrations of As(V), As(III), ROX and ASA were 0.5, 0.5, 1.0 and 1.0 mg L\(^{-1}\), respectively. It was found that the effective treatment volume of MC-1 toward ROX was 288 BVs (2.88 L) (Fig. 12b), in which the maximum permissible
concentration of ROX (29 μg L⁻¹) and removal efficiency of 98.14% were achieved. The adsorption capacity of the MC-1 fixed bed was nearly exhausted up to 3000 BVs (30 L) of continuous inflow of ROX solution (ca. 80 h). The effective treatment volume and the exhaustion volume were subject to the adsorbent loading mass (Zietzschmann et al., 2016). As the outcomes of breakthrough curves were demonstrated in Fig. S18 and Fig. S19, the effective treatment volumes of MC-1 and MC-2 toward ASA, ROX and As(V)

Fig. 7. (a) XPS spectra of C 1s, (b) XPS spectra of O 1s, and (c) XPS spectra of Fe 2p before and after arsenic adsorption (only ROX was shown as an example).

Fig. 8. Proposed interaction mechanism between MIL-88A(Fe) and four different arsenic pollutants.
Fig. 9. The adsorption of (a) ASA, (b) ROX, (c) As(V), and (d) As(III) made up by pure, tap, lake, and rain water on the obtained MC-1 (Initial ASA and ROX concentration: 1 mg L$^{-1}$; Initial As(V) and As(III) concentration: 0.5 mg L$^{-1}$).

Fig. 10. The adsorption of (a) ASA, (b) ROX, (c) As(V), and (d) As(III) made up by pure, tap, lake, and rain water on the obtained MC-2 (Initial ASA and ROX concentration: 1 mg L$^{-1}$; Initial As(V) and As(III) concentration: 0.5 mg L$^{-1}$).
solutions ranged from 252 to 432 BVs (2.52 L–4.32 L). Being compared with the pristine MIL-88A(Fe) particles, MC-1 and MC-2 displayed relatively lower adsorption capacity due to the small absolute amounts of MIL-88A(Fe) in the fixed-bed column. However, the adsorption performances of both MC-1 and MC-2 were still superior to those of the previously reported counterpart (Jun et al., 2015). This observation may be attributed to the uniform distribution and highly stable structure of MIL-88A(Fe)/cotton fibers, which enhances contact efficiency of MIL-88A(Fe) with inorganic and organic arsenic in aqueous solution. The breakthrough curve in other researches usually demonstrated an S shape and fitted well to Yoon–Nelson and Bohart–Adams model, in which the overshoot peak was presented till the adsorption saturation of the adsorbents reached (Xiong et al., 2019). However, in this study, the breakthrough curve was not perfect as theoretical models (Peng et al., 2018). The reason is that the fixed bed column experiments in this study were more closed to practical large-scale operation, which guaranteed the rapid flow of arsenic solution in order to enhance hydraulic loading rate (Ma et al., 2018). Furthermore, the leaking Fe contents in the effluents determined by ICP-
OES were maintained to zero during operation of the water system, implying the MIL-88A(Fe) in both MC-1 and MC-2 was stable and nearly free of Fe leaking to the environment. In all, both MC-1 and MC-2 in fixed bed exhibited great possibility to be used in large-scale operation due to their outstanding adsorptive removal performance toward inorganic and organic arsenic pollutants from the contaminated water samples, stability and eco-environment friendly.

4. Conclusion

In this study, MIL-88A(Fe) with well-crystallized hexagonal microrods have been synthesized via a mild method at room temperature, which exhibited excellent adsorption abilities toward inorganic and organic arsenic pollutants. The maximum adsorption capacities of MIL-88A(Fe) toward As(III), As(V), ROX and ASA was 126.5, 164.0, 261.4 and 427.5 mg g⁻¹, respectively, which was higher than most counterpart adsorbents. The adsorption kinetics and adsorption isotherm of various arsenic species on MIL-88A(Fe) can be described by the pseudo-second-order kinetic model and Langmuir isotherm model, respectively. The outstanding adsorption performances of MIL-88A(Fe) toward different arsenic pollutants can be assigned to the coordinated interactions of As—O—Fe between arsenic pollutants and MIL-88A(Fe). To achieve good recyclability and facile separation, MIL-88A(Fe) was decorated on cotton fibers via both post synthetic method and in-situ growth method to obtain MC-1 and MC-2 composites, which demonstrated identically outstanding removal efficiencies towards inorganic and organic arsenic pollutants in simulated water samples. The fixed-bed column experiments further demonstrated that MC-1 and MC-2 could be potentially used for large-scale removal of arsenic pollutants. This work provided us possibility to weave the cotton fibers decorated with MIL-88A(Fe) into threads and even cloth or web, which was used to capture the arsenic pollutants from the real water system.

Credit author statement


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Appendix A. Supplementary data

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Declarations of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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