

Characteristics of arsenate removal from water by metal-organic frameworks (MOFs)

Jie Li, Yi-nan Wu, Zehua Li, Miao Zhu and Fengting Li

ABSTRACT

Contamination of arsenic in groundwater and surface water occurs frequently across the globe, requiring an effective purification technology. Among the common technologies, the adsorption method is widely used for the merits of low cost and easy operation. Nevertheless, the development of efficient adsorbents remains one of the central challenges in this field. In this article, one kind of typical porous metal-organic framework material (MIL-53(Al)) was explored for the removal of arsenate from water. MIL-53(Al) has a maximum removal capacity of 105.6 mg/g and a conditional capacity of 15.4 mg/g at a low equilibrium concentration (10 µg/L). The optimum initial pH value is 8.0. Except for PO_4^{3-} , other coexisting anions do not show a notable influence on the adsorption capacity of MIL-53(Al). In general, MIL-53(Al) is a promising new material for arsenate removal from water. Investigation of the effects of electrical charges, Fourier transform infrared spectroscopy spectra, and X-ray photoelectron spectroscopy (XPS) spectra revealed that electrostatic attraction and hydrogen bond might be involved in the adsorption process of arsenate onto MIL-53(Al).

Key words | adsorption characteristics, adsorption mechanism, arsenate, MIL-53(Al)

Jie Li
Yi-nan Wu
Zehua Li
Miao Zhu
Fengting Li (corresponding author)
State Key Laboratory of Pollution Control and
Resource Reuse Study,
College of Environmental Science & Engineering,
Tongji University,
1239, Siping Road,
Shanghai 200092,
China
E-mail: fengting@tongji.edu.cn

INTRODUCTION

Arsenic is a highly toxic metalloid element. In recognition of the serious health hazard caused by prolonged exposure to arsenic in the environment, the World Health Organization took the lead to revise the arsenic limits in drinking water from 50 to 10 µg/L in 1993 (Choong *et al.* 2007). Statistics from the International Water Association suggest that more than 200 million people are in varying degrees affected by arsenic pollution caused by natural geochemical processes and human activities. Thus, it is urgent to remove arsenic from contaminated groundwater and surface water. Arsenic mainly exists as inorganic oxyanions in natural water, of which arsenite in trivalent oxidation state (As(III)) is more toxic and difficult to remove than arsenate in pentavalent oxidation state (As(V)). Thus, in practical water treatment processes, oxidation pretreatment of arsenic-contaminated water is often applied to transform arsenite into arsenate because the latter is preferred and easy to remove.

In terms of arsenate-contaminated water, the most commonly used technologies include precipitation, membrane technology, biological processes, and adsorption. Precipitation is often used to treat industrial wastewater with relatively high arsenic concentrations. Membrane

technology is a method with the potential to meet the regulations of drinking water; however, this method requires high treatment cost. Biological processes feature low treatment cost and the absence of secondary pollution but need severe operation conditions. The adsorption method, which is widely used for removing trace contaminants, is an efficient and easy method for purifying micro-polluted water which contains heavy metals and organic pollutants difficult to be biodegraded (Choong *et al.* 2007; Mohan & Pittman 2007). A highly efficient adsorbent is the determining factor in adsorption, and intensive studies have been conducted to synthesize various materials to be applied as adsorbents, such as active carbons, ferric oxide, powdered zeolite, and bio-adsorbents. However, the adsorption capacities of most reported adsorbents are obtained at high initial concentrations (>50 mg/L), and do not represent the actual adsorption performance when treating natural surface water and groundwater that contains trace arsenic. Thus, developing more efficient adsorbents is highly desirable for removing trace pollutants.

Metal-organic framework materials (MOFs), also known as coordination polymers, are metal-organic ligand compounds

that extend via covalent bonding and constitute an emerging class of porous materials (Rowell & Yaghi 2004). Characterized by high surface area, hydrothermal and chemical stability, functionality, and tunability of the pore size, MOFs are potentially applied in gas storage, catalysis, luminescence, separation of organics, and molecular recognition (Czaja *et al.* 2009). However, using MOFs as adsorbents for aquatic arsenate removal has not been reported. In our study, several kinds of typical MOFs prepared by a synthetic route, which involved cheap material, easily controlled reaction conditions and higher yield, and having great potential for mass production were used to test their removal efficiency. Eventually, $\text{Al}(\text{OH})(\text{O}_2\text{C}-\text{C}_6\text{H}_4\text{CO}_2)$ (MOF: MIL-53(Al)) was found to be the best and was selected in this study as adsorbent to eliminate aquatic arsenate (Loiseau *et al.* 2004; Qian *et al.* 2013). Adsorption performance was systematically studied with respect to pH effects, kinetics, isotherms, and effect of the coexisting anions. Surface charge potential, Fourier transform infrared spectroscopy (FTIR) spectra, and X-ray photoelectron spectroscopy (XPS) spectra were obtained to examine the possible concerned mechanism.

METHODS

Materials and synthesis

Terephthalic acid (H_2BDC), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and N,N -dimethylformamide (DMF) were purchased from Alfa Aesar. $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$ was supplied by Sinoreagent. All solvents and chemicals are of reagent quality and were used without further purification. De-ionized water was used throughout this work.

H_2BDC (1.245 g) and 4.220 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were added into a mixture of 20 mL H_2O and 55 mL DMF, and stirred at 80°C until H_2BDC and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were completely dissolved. The suspension was heated in an oven at 130°C for 48 h. The obtained white precipitates were collected by centrifuge and washed with de-ionized water and DMF. Finally, the sample was dried under vacuum at 80°C for 24 h for further use, referred to hereafter as MIL-53(Al).

As(V) solution (mg/L level) with different initial concentration was prepared by dissolving $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$ in de-ionized water. Arsenate solution ($\mu\text{g/L}$ level) was prepared by diluting the solution of known concentration. The initial concentration of all these solutions was determined

by an inductively coupled plasma (ICP) spectrometer before batch experiments.

Batch experiments

All experiments were conducted at room temperature (25°C). The adsorbent dosage was 20 mg/L and the pH was adjusted by 1.0 M HNO_3 and 1.0 M NaOH solutions. The arsenic concentration was determined using an ICP spectrometer (Agilent 720ES, USA) at ppm level or ICP-mass spectrometry (Agilent 7700, USA) at ppb levels. Batch experiments were conducted to examine the pH effect, adsorption kinetics, isotherms, and effect of coexisting anions. Classic adsorption models were used to describe the adsorption data: pseudo-first-order and pseudo-second-order models for adsorption kinetic fitting; Langmuir and Freundlich models for adsorption isotherm fitting (Dou *et al.* 2013).

Material characterization

The crystal structure of the adsorbent was obtained by an X-ray powder diffractometer (D8 Advance, Germany). The surface charges of the adsorbents (Zeta potential) at different pH were measured by a zeta potential analyzer (Zetasizer Nano ZS 90, UK). The IR spectra of the adsorbent before and after adsorption were recorded on a FTIR spectrophotometer (Nicolet 5700, USA) from 400 cm^{-1} to $4,000\text{ cm}^{-1}$ under ambient conditions. The adsorbent samples before and after arsenate adsorption were analyzed using an X-ray photoelectron spectroscope (AXIS Ultra DLD, Kratos, Japan) with a 1,486.6 eV $\text{Al K}\alpha$ X-ray source. The energy step size for the wide-scan spectra was 1 eV. All binding energies were calibrated with neutral C1s at a binding energy of 284.6 eV.

RESULTS AND DISCUSSION

Characterization of the material

As shown in Figure 1, the characteristic peaks of both pristine and arsenate-loaded material matched well with the simulation peaks previously reported (Zhou *et al.* 2013), suggesting the stability of the crystal structure. The surface area of the synthesized MIL-53(Al) was $920\text{ m}^2/\text{g}$. In addition, no aluminum ion was detected after the adsorption experiment, ensuring the safety of using this material for application in drinking water treatment. In conclusion, the

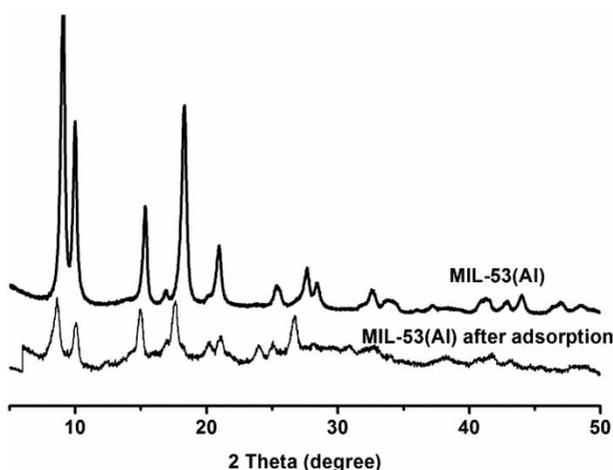


Figure 1 | X-ray diffraction patterns of the synthesized material before and after adsorption.

synthesized material was an excellent candidate for an efficient adsorbent.

Adsorption kinetics

Figure 2 shows the adsorption kinetics of As onto the synthesized material. The adsorption rate was initially high, reaching 80% of its maximum adsorption capacity within 11 h, and slowed down gradually in the following steps. Consequently, a reaction time of 24 h was selected for further batch experiments on MIL-53(Al). Among the classic adsorption kinetic models, the pseudo-second-order model was more suitable than the pseudo-first-order model to describe the experimental data ($R^2 = 0.987$). The corresponding model assumes electron transfer or sharing between the adsorbate and adsorbent, and that the uptake

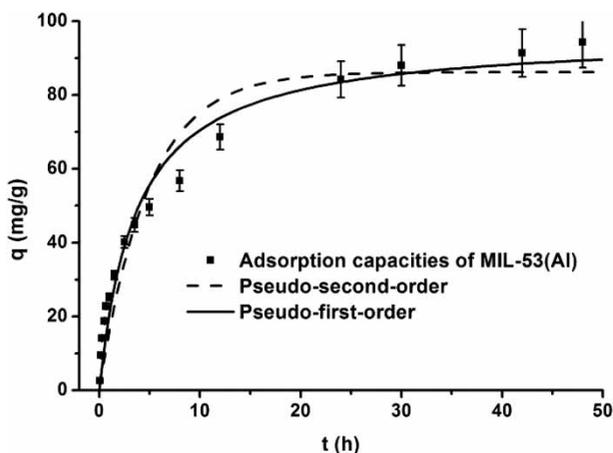


Figure 2 | Kinetics of As(V) adsorption on MIL-53(Al).

rate is controlled by not only adsorbate concentration but also the surface properties of the adsorbent (Ho 2006).

Effects of pH

Figure 3 reveals the adsorption capacity at various initial pH values. For pH between 6 and 9, MIL-53(Al) exhibited a relatively high adsorption capacity and reached a maximum value at pH 8.0. The adsorption capacity of MIL-53(Al) gradually decreased in strong acidic or alkaline conditions. For the adsorbent, reduction of pH changed the surface potential of MIL-53(Al) from negative to positive, which is beneficial to the adsorption of negatively charged pollutants. In terms of the adsorbate, arsenic is multivalent and exists in -3 , 0 , $+3$, and $+5$ oxidation states. Two inorganic forms are common in natural water: arsenite ($+3$, AsO_3^{3-}) and arsenate ($+5$, AsO_4^{3-}). The arsenic speciation is controlled by the redox potential (Eh) and pH value: pentavalent species (H_3AsO_4 , $\text{pH} < 3$; H_2AsO_4^- , $3 < \text{pH} < 6$; HAsO_4^{2-} , $8 < \text{pH} < 10.5$; AsO_4^{3-} , $\text{pH} > 11$) predominate in aerobic environments; trivalent species (H_3AsO_3 , $\text{pH} < 9.2$; H_2AsO_3^- , $9 < \text{pH} < 12$; HAsO_3^{2-} , $12 < \text{pH} < 13$; AsO_3^{3-} , $\text{pH} > 13$) predominate in reducing environments (Mohan & Pittman 2007). For arsenic removal in natural surface water (Eh ≈ 0.4 V) and groundwater after the oxidation pretreatment, both of which are in an aerobic environment, the main concern focuses on the removal of arsenate and the effect of negative charges of arsenate species at various pH ranges. The amount of negative charge of arsenate reduced from three to one upon the pH reduction from 11 to 3, which has an adverse effect on electrostatic attraction (Sharma & Sohn 2009; Chen et al. 2013). These two opposite

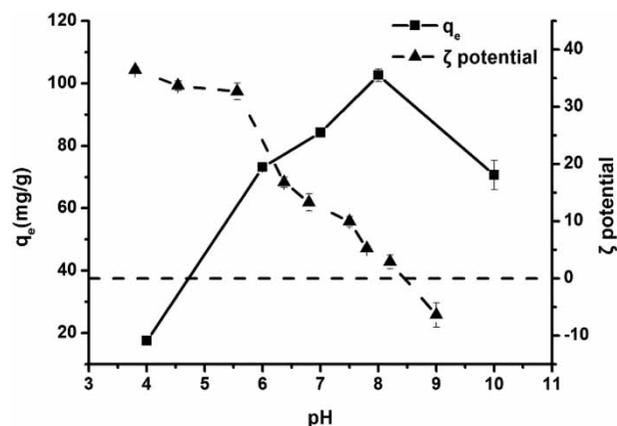


Figure 3 | Effect of pH on the adsorption capacity (q_e) of MIL-53(Al). Full line represents the adsorption capacity, and the dashed line represents the surface charge potential.

effects from the adsorbent and adsorbate respectively were compromised and yielded an optimum pH of around 8.0, implying that electrostatic attraction was a key factor during the adsorption process.

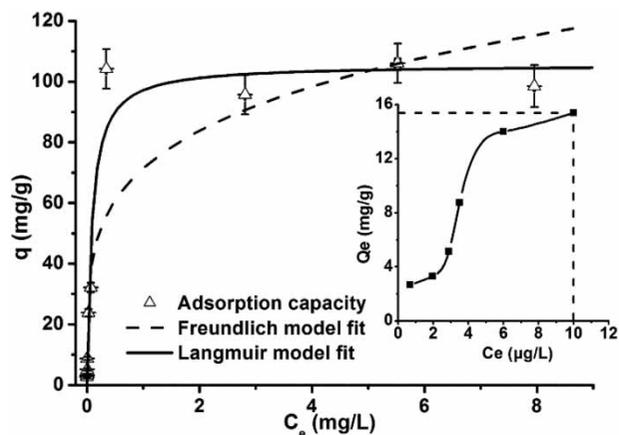


Figure 4 | Adsorption isotherms of As(V) onto MIL-53(Al). Full and dashed lines represent the Langmuir and Freundlich models, respectively. The inset shows the high-resolution isotherm at extremely low equilibrium concentrations.

Table 1 | Adsorbed quantity of arsenate under condition of different equilibrium concentration

Initial concentration (mg/L)	Equilibrium concentration ($\mu\text{g/L}$)	Adsorbed quantity of arsenate (mg/g)	Maximum adsorption capacity (mg/g)
0.054	0.68	2.66	105.6
0.068	1.97	3.30	105.6
0.105	2.88	5.12	105.6
0.318	9.94	15.40	105.6
0.501	24.34	23.84	105.6
0.711	66.93	32.18	105.6
2.428	343.28	104.22	105.6

Table 2 | Comparison of the adsorption capacities of arsenate on various adsorbents

Adsorbent	Equilibrium concentration	Capacity (mg/g)	Reference
Fe_3O_4 nanocrystals	7.8 $\mu\text{g/L}$	0.98	Yavuz <i>et al.</i> (2006)
Nano Fe–Cu binary oxide	9.7 $\mu\text{g/L}$	37	Zhang <i>et al.</i> (2013)
Powder Ce–Ti adsorbent	10 $\mu\text{g/L}$	7.5	Li <i>et al.</i> (2010b)
Granular Ce–Ti adsorbent	10 $\mu\text{g/L}$	2.5	Li <i>et al.</i> (2010b)
Granular ferric hydroxide	10 $\mu\text{g/L}$	8	Badruzzaman <i>et al.</i> (2004)
Iron-oxide-coated quartz	7.43 $\mu\text{g/L}$	0.05	Mostafa <i>et al.</i> (2010)
MIL-53(Al)	10 $\mu\text{g/L}$	15.4	This study
MIL-53(Al)	0.34 mg/L	105.6	This study
Polyaluminum granulate	7.5 mg/L	15	Mertens <i>et al.</i> (2012)

Adsorption isotherms

Figure 4 illustrates the adsorption isotherm with fitting models. The high correlation coefficient suggested that the Langmuir model, which assumes uniform surface monolayer adsorption behavior (Li *et al.* 2010a; Zhao *et al.* 2010), was suitable for describing As(V) adsorption onto the adsorbents. The removal capacity of MIL-53(Al) obtained from the Langmuir model was 105.6 mg/g, which was consistent with the experiment results.

The corresponding fitting model can directly yield the maximum adsorption capacity of different materials. But the maximum adsorption capacity is not equal to the conditional removal capacity or the quantity of the adsorbed arsenate for the difference in water quality. Among the factors, including pH value, reaction time and coexisting anions, initial (equilibrium) concentration is the key factor. Table 1 compares the conditional removal capacity of MIL-53(Al) with different initial (equilibrium) concentrations. Despite the normal concentration of arsenate in natural water (50–200 $\mu\text{g/L}$), only with much higher initial (equilibrium) concentration could the maximum adsorption capacity be obtained. The consequence is the disparity between the maximum and conditional adsorption capacity in a practical water treatment process. Therefore, more objective comparison shall be made under condition of the same equilibrium concentration instead of directly comparing the maximum adsorption capacity. The inset of Figure 4 shows the isotherms of MIL-53(Al) within low equilibrium concentrations. At an equilibrium concentration of 10 $\mu\text{g/L}$ (the safety limits for arsenic in drinking water set by the World Health Organization), MIL-53(Al) exhibited a removal capacity of 15.4 mg/g, which is higher than some other adsorbents previously reported (Table 2).

In general, MIL-53(Al) outperformed the other adsorbents in terms of both the maximum removal capacity and the adsorbed amount of arsenate at low equilibrium concentration.

Effect of coexisting anions

In addition to enormous discrepancies in pollutant concentrations among laboratory studies and natural water sample, the existence of coexisting anions is another key factor that influences the actual removal capacity in practice. In this section, several coexisting anions (Cl^- , F^- , NO_3^- , SO_4^{2-} , and PO_4^{3-}) were selected to analyze their effects on adsorption capacity (Figure 5). The conditional removal capacity only maintained 13.5% of the maximum adsorption capacity in the presence of PO_4^{3-} (0.02 mol/L) for the similar nature of PO_4^{3-} and AsO_4^{3-} and their competition for binding sites. Other anions did not show a noteworthy influence on the performance of MIL-53(Al). Overall, MIL-53(Al) performed well in the presence of coexisting anions.

Mechanism discussion

FTIR and XPS were used to investigate the surface interactions between the adsorbent and adsorbate. Figure 6(a) illustrates the FTIR spectra of pristine and As-loaded adsorbent. The primary peaks matched well with the previously reported FTIR spectra of MIL-53(Al) (Loiseau *et al.* 2004, Park *et al.* 2006). Pristine and As-loaded MIL-53(Al) exhibited vibration bands at 1,400–1,700 cm^{-1} for the carboxylic functional group (Rallapalli *et al.* 2010). After

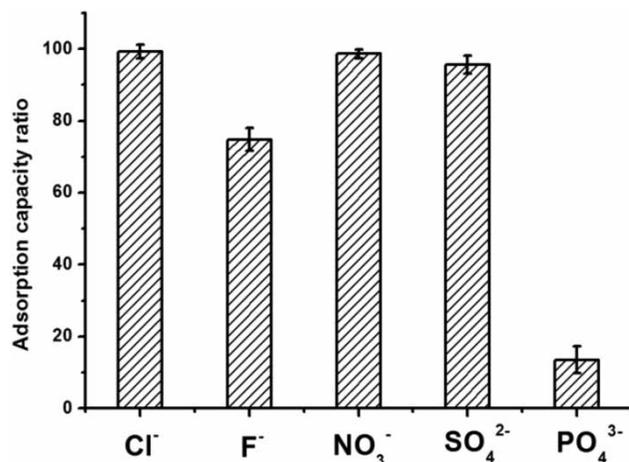


Figure 5 | Effects of anions on adsorption capacities of MIL-53(Al).

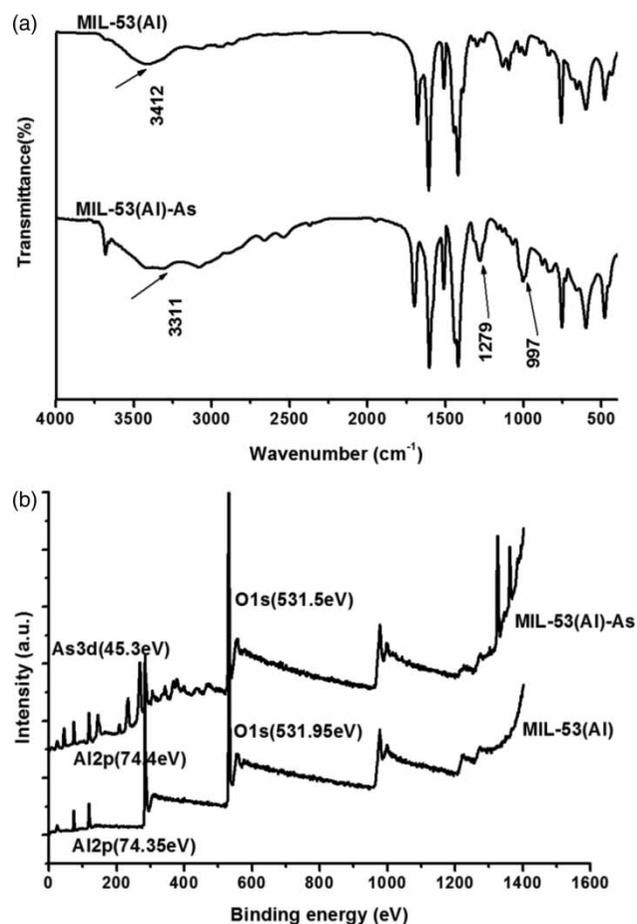


Figure 6 | FTIR and XPS spectra of MIL-53(Al) before and after adsorption.

adsorption, two broad peaks occurred at 1,297 and 997 cm^{-1} , which are attributed to the overlapped adjacent peaks. The peak at 997 cm^{-1} could be assigned to the overlapped peaks at 965 and 1,125 cm^{-1} , corresponding to the bending vibrations of the hydroxyl group in the trans corner-sharing octahedral $\text{AlO}_4(\text{OH})_2$ and those in hydrogen bonds with the guest molecules, respectively (Volklinger *et al.* 2009). The peak at 3,412 cm^{-1} shifted to 3,311 cm^{-1} and became significantly broad, suggesting that the hydroxyl groups were involved during adsorption and the hydrogen bonds might be related. The absence of a clear As–O band at about 800 cm^{-1} was caused by the predominance of other intense absorption peaks.

The XPS spectra were obtained for the adsorbent before and after As(V) adsorption. The wide-scan spectra (Figure 6(b)) revealed that some arsenic atoms were detected on the adsorbent surface after adsorption, confirming the successful adsorption of arsenate on both adsorbents. Among the binding energy peaks, the binding

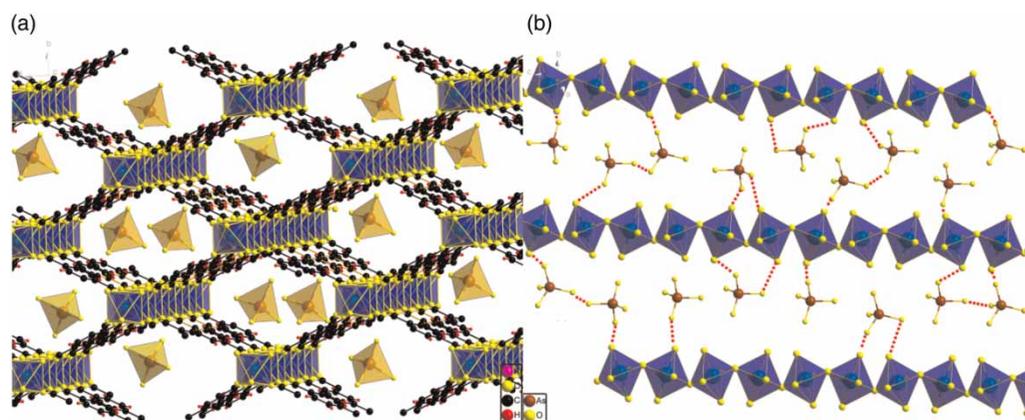


Figure 7 | Simulated locations of arsenate molecules in MIL-53(Al) viewed from different directions: (a) along the crystallographic z direction; all metal ions and arsenate are present as the polyhedral; (b) along the x direction; metal ions are present as the polyhedral and arsenate as the ball and stick model. Arsenate molecule is linked through hydrogen-bonding interactions (represented by red dashed line). Color scheme: Al, pink; O, yellow; C, dark; H, red; and As, brown.

energies for the O1s peak gradually decreased from 531.95 to 531.5 eV because arsenate anions contain some hydroxyl groups which have a lower binding energy compared to the coordinated oxygen atoms.

CONCLUSIONS

In this study, MIL-53(Al) was prepared for the adsorption of arsenate from water and some useful information about the characteristics of arsenate removal by MIL-53(Al) was provided. The adsorption kinetics data fitted better with the pseudo-second-order model than the pseudo-first-order model, and the maximum capacity could be basically reached within 11 h. In neutral pH range (6–8), MIL-53(Al) exhibited a relatively high adsorption capacity and reached a maximum value at pH 8.0. MIL-53(Al) outperformed the other adsorbents in terms of both the maximum removal capacity (105.6 mg/g) and the capacity obtained at low equilibrium concentration (15.4 mg/g at 10 µg/L). Except for PO_4^{3-} , other coexisting anions did not show a noteworthy influence on the adsorption capacity of MIL-53(Al). In addition, the structure of MIL-53(Al) was maintained and no aluminum ion was detected after the adsorption experiment, ensuring the safety of using this material for application in drinking water treatment. In conclusion, MIL-53(Al) is an effective adsorbent for arsenate removal from water. The FTIR and XPS spectra, as well as the investigation of pH effects on the adsorption, revealed that electrostatic attraction and hydrogen bond might be involved in the adsorption process of arsenate onto MIL-53(Al) (Figure 7).

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