Mono-, Di-, and Tricarboxylic Acid Facilitated Lanthanum-Based Organic Frameworks: Insights into the Structural Stability and Mechanistic Approach for Superior Adsorption of Arsenate from Water

Subbaiah Muthu Prabhu, Shunsuke Imamura, and Keiko Sasaki*

Department of Earth Resources Engineering, Kyushu University, Fukuoka 819-0395, Japan

ABSTRACT: In this study, we tried to synthesize lanthanum organic frameworks (MOFs) with the linkers of benzoic acid (BA), 1,4-benzenedicarboxylic acid, and 1,3,5-benzenetricarboxylic acid (BTC), abbreviated as La-BA, La-BDC, and La-BTC, respectively. Interestingly, the BA linker approached La metal to form lanthanum methanoate (La(HCOO)₃) instead of the La-BA MOF through an acid catalyst amide-hydrolysis mechanism, whereas La-BDC and La-BTC act as MOFs, confirmed by PXRD patterns. Various sophisticated instrumentation techniques such as FTIR, PXRD, XPS, BET, and TGA were utilized to understand the formation of MOF. This is the first report to investigate AsO₄³⁻ adsorption and the dissolution behavior of La-BA, La-BDC, and La-BTC in detail using different spectroscopic methods. The maximum AsO₄³⁻ adsorption densities obtained from the Langmuir isotherm model were found to be 2.623, 3.891, and 0.280 mmol/g for La-BA, La-BDC, and La-BTC, respectively, where the dose ratio was 1 g/L with the speed of 100 rpm at room temperature. The value for La-BDC was significantly superior to the previously reported adsorbents for AsO₄³⁻ to date. The presence of AsO₄³⁻ on both La-BA and La-BDC was confirmed by FTIR and XPS As 3d. After adsorption of 2.4 mM AsO₄³⁻, the precipitation mechanism controls the adsorption capacities on La-BA and the ligand exchange mechanism on La-BDC confirmed by solution as well as solid analyses. Sorption kinetic data of AsO₄³⁻ followed a pseudo-second-order model, which is consistent with chemisorption involving the possible coordination of AsO₄³⁻ on La-BA and La-BDC. These results suggested that the MOF materials can be developed to immobilize arsenic-rich wastewater.

KEYWORDS: Metal organic frameworks, Lanthanum, Arsenate, Adsorption, Ligand exchange

INTRODUCTION

In natural water, arsenic (As) predominately occurs in two forms i.e., arsenite (AsO₃³⁻) and arsenate (AsO₄³⁻), in which AsO₃³⁻ is highly dangerous due to its mobility and toxicity. As concentration in drinking water is considered to be a serious global environmental issue due to its toxicity and carcinogenicity. The acceptable concentration of As in drinking water is 10 μg/L, set by the World Health Organization (WHO). Of all the existing techniques, adsorption is shown to be more attractive and is traditionally used because of its greater efficiency, inexpensive expenditure, and simplicity.[1-6]

A new kind of material, namely, metal organic framework (MOF) and its based composites, was highly exposed in the fields of energy and environmental science, as they are potentially porous compounds formed by the linking of inorganic and organic units through coordinative bonding.[7] Recently, Zr-based MOFs/composites showed good performance toward the removal of toxic ions from water. Wang et al. proposed UiO-66 as the superior adsorbent for AsO₄³⁻ adsorption (303 mg/g).[8] Fe-BTC MOF was synthesized via a simple solvothermal method which exhibited a high uptake capacity for AsO₄³⁻ of 12.287 mg/g.[9] Zeolitic imidazolate framework-8 for the removal of trace amounts of AsO₄³⁻ from water was described by Li et al., showing a maximum AsO₄³⁻...
uptake capacity of 76.5 mg/g.\textsuperscript{10} Followed by Fe-BTC, MIL-53(Fe) (Fe-BDC) was synthesized and it showed higher uptake performance toward AsO\textsubscript{4}\textsuperscript{3−} (21.27 mg/L) than the Fe-BTC.\textsuperscript{11} Though, in the literature there are many studies of toxic AsO\textsubscript{4}\textsuperscript{3−}/AsO\textsubscript{3}\textsuperscript{3−} removal using iron-based materials, La-based materials have shown higher adsorption density than Fe(III)-based materials due to the affinity of lanthanum, which is much higher than iron. Also, Fe(III)-arsenate was less stable and showed higher solubility of the product (K\textsubscript{sp}) (5.7 × 10\textsuperscript{−21}) than La-arsenate, (1.07 × 10\textsuperscript{−21}). This means that the iron is easily released from the structure after adsorption of AsO\textsubscript{4}\textsuperscript{3−} and is less suitable for drinking water and also it needs substantial methods to stabilize the materials, which in turn increase the cost factor. However, a limited number of studies were performed with La/La-based composites for the removal of toxic As. Moreover, La\textsuperscript{3+}-encapsulated materials have been demonstrated to be the most effective materials for toxic ion removal in the literature owing to their specific affinity.\textsuperscript{12,13} In addition, La\textsuperscript{3+} is considered as an inexpensive abundant rare earth element with excellent biocompatibility as well as an environmentally benign material.\textsuperscript{14} Nevertheless, until now, La-based MOFs have been hardly reported in the literature. Recently, the calcined form of La (1,3,5-benzene tricarboxylic acid) was utilized for phosphate adsorption from water by Zhang et al. The maximum adsorption capacity of phosphate on La(1,3,5-BDC) was 10 mg/g.\textsuperscript{15} Until now, there had been no report for how the metal−organic linker interaction was formed and the role of DMF in structure elucidation.

The main aim of this present work is to prepare La-based MOFs such as La-BA, La-BDC, and La-BTC MOFs for the immobilization of AsO\textsubscript{4}\textsuperscript{3−}. The synthesized La-based materials were characterized well by FTIR, PXRD, TGA, BET, SEM, and BET to understand the mechanism of formation of MOF/MOF-like materials and to examine the high concentration of AsO\textsubscript{4}\textsuperscript{3−} removal by batch experiments. The influence of time, pH, coexisting anions, and different initial concentration studies on the adsorption capacity was also investigated in detail. The synthesized materials exhibited high adsorption densities and were applicable for wide pH ranges, making them for an excellent material for the removal of toxic AsO\textsubscript{4}\textsuperscript{3−} from water.

### EXPERIMENTAL SECTION

**Materials.** Benzoic acid (BA), 1,4-benzenedicarboxylic acid (BDC), 1,3,5-benzene tricarboxylic acid (BTC), lanthanum nitrate hexahydrate (La(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O), potassium arsenate (KH\textsubscript{2}AsO\textsubscript{4}), dimethylformamide (DMF), and ethanol) were purchased from Wako Chemicals, Japan. All chemicals were used as received without further purification. Milli-Q water (18.2 MΩ) was used for solution preparation and synthesis, and 2.3 mM AsO\textsubscript{4}\textsuperscript{3−} stock solution was prepared by dissolving the proper amount of KH\textsubscript{2}AsO\textsubscript{4} in Milli-Q water.

**Synthesis of La-BA, La-BDC, and La-BTC.** The La-BDC MOF was synthesized by the solvothermal method based on the previous studies.\textsuperscript{8,16} 743 mg (2 mmol) of La(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O and 250 mg (2 mmol) of BDC were dissolved in DMF (70 mL) and sonicated for 5 min for complete dissolution. The reaction was stirred for 30 min magnetically, and then the mixture was placed in a 100 mL Teflon-lined stainless steel autoclave at 120 °C for 24 h. After 24 h reaction, the autoclave was cooled down to room temperature and the powdery product was collected. The MOF materials were washed with reaction solvent first to remove any unreacted BDC moieties. Successively, the reaction product was washed with ethanol 3−4 times to replace the reaction solvent. The obtained slurry was vacuum-dried for 24 h at 80 °C. Then, the product was water washed to remove any unreacted lanthanum species and freeze-dried. A similar procedure has been followed for the synthesis of La-BA and La-BTC with BA and BTC linkers, respectively.

**Adsorption Experiments.** For the batch adsorption experiment, 40 mg of the adsorbent was added to 40 mL of 2.4 mM KH\textsubscript{2}AsO\textsubscript{4} and the mixture was shaken thoroughly at 100 rpm at 25 °C. After the reaction the adsorbent was separated by filtration and the equilibrium concentration of AsO\textsubscript{4}\textsuperscript{3−} was analyzed by ICP-OES (Optima 8300, Thermo Scientific, USA).
PerkinElmer Co., Ltd., Yokohama, Japan). The influence of pH and coexisting anions and natural organic matter on the adsorption of AsO$_4^{3-}$ was investigated in detail. The kinetics of AsO$_4^{3-}$ adsorption were examined under similar conditions by withdrawing samples at time intervals. The solution was later filtered to determine the residual arsenic and lanthanum concentrations using ICP-OES. All adsorption results were expressed as the average of duplicate measurements.

**RESULTS AND DISCUSSION**

**Adsorbents Characterization.** The structural integrity after the introduction of organic ligands on La metal was examined by PXRD patterns. When the ligand BA was complexed with La, it did not form a La-BA MOF but instead formed lanthanum methanoate [La(HCOO)$_3$] (JCPDS 00-018-0674) through an acid-catalyst amide hydrolysis approach, as shown in Scheme 1. The BA has an important role for the development of [La(HCOO)$_3$] as well as La(OH)$_3$. First, in this reaction, the BA ligand acts as a Lewis acid, which protonates the amide carbonyl of DMF, which deprotonates the oxonium ions to carboxylic acid to formic acid as the main product (1c) and the deprotonation of the oxygen ions to carboxylic acid as the main product (1e). Second, the BA considerably influenced the growth of La(OH)$_3$ crystals by chelation, as it has one $\equiv$COOH group. The carboxylic groups control the growth and particle distribution of the metals and as a result, a rodlike crystal morphology of the product was obtained. Likewise, the different organic acids not only influence the product shapes but also their crystallinities. The La(OH)$_3$ crystals were synthesized via the citric-acid assisted hydrothermal method by the Tang et al. group, where the citric acid acted as protective agent to control the growth rate of crystals in different directions as follows. The formation of the stable lanthanum-citrate complex was further hydrolysis to produce colloidal La(OH)$_3$ nanoparticles capped with citric acid, and it controls the growth rate of the La(OH)$_3$ nanoparticles. A similar phenomenon was applied here instead of citric acid; BA was utilized to control the growth rate of La(OH)$_3$. Further, the BA capped La(OH)$_3$ nanorods were reacted with formic acid to form a lanthanum methanoate (1d) as the final product. In the case of BDC and BTC ligands with La, the highly crystalline MOFs, La(1,4-BDC) (JCPDS: 00-034-1984) and La(1,3,5-BTC) (JCPDS: 00-023-1746), were obtained. As the BDC and BTC ligands have two and three carboxylate groups, respectively, they could act as not only the ligands with La but also linkers to extend the clusters of the MOF (Figure 1).

The formation of La-BA, La-BDC, and La-BTC with their respective ligands was confirmed by FTIR spectra (Figure 2). In the case of La-BA, the $\text{OH}$ stretching vibration mode occurred at 3426 cm$^{-1}$. The peaks at 2920 and 1426 cm$^{-1}$ are assigned to $\nu\text{CH}$ stretching and it is the corresponding bending vibration mode, respectively, confirming the presence of the methanoate structure of La(OH)$_3$ facets and a sharp peak at 778 cm$^{-1}$ suggesting the presence of benzene ring $\equiv$C–H bending vibration mode of BA, in which a small amount of BA was still present in the structure. The narrow intense peak at 1426 cm$^{-1}$ is attributed to $\text{–C}\equiv\text{O}\text{–C}\equiv\text{O}$. A small peak positioned at 432 cm$^{-1}$ is due to the stretching vibration mode of the La–O bond. The La–OH moiety also reveals the peaks present at the wavenumbers of 660 and 512 cm$^{-1}$. Although La-BA was confirmed as La(HCOO)$_3$, by PXRD, the presence of the $\nu\text{CH}$ stretching vibration mode confirms the presence of a few benzoic acid and/or dimethyl amine groups, which are selectively bound to specific crystallographic facets of the La-BA surface.

The La-BDC spectrum indicated the peak at 3423 cm$^{-1}$ is ascribed to the $\nu\text{OH}$ stretching vibration mode of the BDC linker, and the peaks at 1588, 1536, and 1400 cm$^{-1}$ correspond to the vibration modes of the aromatic carbons. The C–H bending vibration mode appeared at 1310 cm$^{-1}$. The peaks at 1153 and 1019 cm$^{-1}$ were identified as C–N and C–O stretching vibration modes from DMF, suggesting that the presence of a small amount of DMF molecules occupied the surface of the La-BDC, and this statement is supported by previous studies. The sharp peaks at 756 and 512 cm$^{-1}$ suggest the modes of benzene ring C–H bending vibration and La–O bending vibrations, respectively. After the formation of the La-BTC MOF, no other significant peaks were obtained because the similar functional groups were present in BTC.

Figure 3 shows the TGA profiles of the synthesized products along with the standard La(OH)$_3$ as reference. The reference La(OH)$_3$ showed a very small degradation at 100–200 °C, due
to the water evaporation, confirming that there is no moisture in the products. The next decomposition starts at 310 °C due to the transformation of La(OH)₃ to La₂O₃ through La₂O₂CO₃ over 480 °C, and this statement is confirmed from our previous report.²³ For La-BDC, in contrast, the first degradation occurred between 150 and 230 °C and is due to the trace amount of DMF evaporation from the structure. The next degradation interval on La-BDC at 330 °C is due to the decomposition of ligands which are coordinated to metal ions. The TGA results indicate that La-BDC possesses significantly higher thermal stability compared with the other La-BA clusters, indicating that the BA ligand was not coordinated to the La atoms. In the case of La-BTC, the main degradation started at 350 °C due to the BTC molecules,²⁴ and the final degradation at 645 °C was due to the coordinated bonding between the lanthanum and the carboxylate groups in a similar manner to La-BA and La-BDC.

Figure 4 shows the SEM images of as-prepared La-BA and La-BDC products, showing that a large quantity of nanorods were successfully formed in the case of La-BA. Also, the BA moiety acted as capping agent as well as protective layer to control the growth of La(OH)₃ particles, which results in the nanorods morphology of La-BA being obtained. In addition, BA is also known as a modulator for the synthesis of UiO-66-based materials. The small amount of dimethyl amine as a minor product also disturbs the formation of the uniform structure of La-BA nanorods. The SEM image of La-BDC MOF shows that this bulk solid interconnected structure is composed of clustered lanthanum and BDC-linkers. This is totally different from La-BA, suggesting the formation of a MOF but not any oxides/carbonates, which has a different morphology than is shown in the literature.²⁵ However, the La-BTC MOF also shows a rodlike structure similar to aggregated La-BA. Similarly, Shang et al. reported the formation of a needle-like La(1,3,5-BTC) MOF using an ionic liquid-assisted microemulsion technique.²⁶

The BET specific surface areas (SSAs) were approximately 3.50, 5.30, and 12.6 m²/g for La-BA, La-BDC, and La-BTC, respectively, and their average pore sizes are as shown in Table 1. The final products were dissolved in 1 M HNO₃ to calculate the atomic molar ratio of La-BA and La-BDC. The presence of C, N, and H and their molar ratios were calculated using CHN analyses as shown in Table 1. The presence of a trace amount of N from DMF also participated in the adsorption of AsO₄³⁻ via coordination for the La-BDC MOF. However, La-BA does not have any DMF molecules, clearly depicting the formation of formic acid which further converted into lanthanum methanoate with La(OH)₃.

Figure 5a shows the wide XP spectrum of La-BA. The high-resolution C 1s spectrum of La-BA is further divided into two main components with respect to the formic acid structure of C−C/C−H and O=C=O. A peak at Eₛ[c 1s] = 284.6 eV is attributed to the C=C from the BA moiety; the O=C=O peak detected at Eₛ[O 1s] = 288.2 eV is primarily contributed by the methanoate groups, as they have only C−C/C−H and COO⁻ groups in the structure. Additionally, the La-BA sample shows two component peaks at 529.4 and 531.6 eV for Eₛ[B] = 531.6 eV on the surface of the material might be from the methanoate rather than the BA material (Figure 5c). The La 3d peaks further divided into the doublets of La 3dₓᵧ and La 3dₓ/₂ at 873.0 and 853.3 eV, respectively.²⁷,²⁸ The difference between the La-doublets is 16.5, which is close to the theoretical value 16.4 eV of the standard La(OH)₃ pattern.

For, La-BDC, the wide spectrum shows the photoelectron spectrum lines at 862, 556, and 310 eV, corresponding to C 1s, O 1s, and La 3d, respectively (Figure 6a). The C 1s of La-BDC consists of three different chemically shifted components observed by a deconvolution as −C−C=, C=O, and −COO=, with their corresponding Eₛ[C 1s] = 284.6, 286.4, and 290.3 eV, respectively (Figure 6b).²⁹ The ratios of carbon in carboxyl, aromatic alkene, and aromatic alkane

Figure 3. TGA profiles of the synthesized La-based products with std. La(OH)₃ as reference. (conditions: Temp. 25 to 1000 °C with the heating rate of 10 °C/min).

Figure 4. SEM images of La-BA, La-BDC, and La-BTC products. Scale bars at 2 μm.
groups from the BDC group were found to be 1:2:1, as shown in the structure in the mechanism part later. As expected, the area ratio of the above groups is found to be the same. The peaks at $E_{\text{B}[\text{O 1s}]} = 530.2$, 531.6, and 533.1 eV are due to the $\text{La}^-$-$\text{O}$ bond, free $-\text{OH}$, and $\text{C}=\text{O}$ groups (Figure 6c) on the sample surfaces, respectively. In this case, the carboxylate concentration is relatively higher than hydroxyl groups, and hence, the intensity of carboxylate oxygen is higher than that of hydroxyl oxygen. In the 3d core level photoelectron spectra for $\text{La}$ in $\text{La-BDC}$, the peaks observed at 838.0 and 854.4 eV correspond to the $\text{La}$ 3d$_{5/2}$ and $\text{La}$ 3d$_{3/2}$ orbitals, respectively, which are similar to the $\text{La-BA}$ (Figure 6d). The difference in $E_{\text{B}}$ between $\text{La}$ 3d$_{3/2}$ and $\text{La}$ 3d$_{5/2}$ was fixed to 16.4 eV. For the $\text{La}$ species in $\text{La-BA}$ and $\text{La-BDC}$, the latter part has higher binding energy than $\text{La-BA}$ due to the presence of the bulky BDC group, whereas the $\text{La-BA}$ part has a smaller methanoate group with $\text{La}$.

**Effect of pH.** $\text{La-BA}$ and $\text{La-BDC}$ MOF can be applied in practical $\text{AsO}_4^{3-}$ removal from water. It was found that the adsorption capacity of $\text{AsO}_4^{3-}$ on both $\text{La-BA}$ and $\text{La-BDC}$ did not have obvious differences in the wide pH from 3 to 10, as shown in Figure 7a. The $\text{AsO}_4^{3-}$ adsorption capacity at pH 2 was very low due to the partial dissolution of $\text{La}$ species from $\text{La-BA}$ and $\text{La-BDC}$ MOFs. Also, at pH 2, the dominant arsenate species is present in the molecular form ($\text{H}_3\text{AsO}_4$) and delivers no electrostatic attraction. The adsorption density of $\text{AsO}_4^{3-}$ is very low at pH 12 due to the presence of a very high concentration of hydroxyl ions. After the adsorption of 2.3 mM $\text{AsO}_4^{3-}$ on $\text{La-BA}$, the methanoate molecules were replaced by arsenate ions. This formed lanthanum arsenate as a stable final product, confirmed by the PXRD pattern (JCPDS: 01-076-4590). The formic acid is categorized as a good leaving group as it has a $pK_a$ of 3.77, compared to $\text{AsO}_4^{3-}$, which has a value of 9.2. It is worth mentioning that the release of the formic acid group is reasonable for lowering the equilibrium pH of the solution, which favors enhancing the adsorption of $\text{AsO}_4^{3-}$ over the pH range. To confirm the formation of lanthanum arsenate on lanthanum, we carried out

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>BET SSA (m$^2$/g)</th>
<th>Avg. pore size (nm)</th>
<th>C</th>
<th>N</th>
<th>La</th>
<th>C/La</th>
<th>As/La</th>
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<tr>
<td>$\text{La-BA}$</td>
<td>3.50</td>
<td>29.02</td>
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<td>3.731</td>
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<td>$\text{La-BDC}$</td>
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<td>21.42</td>
<td>23.950</td>
<td>0.433</td>
<td>1.936</td>
<td>12.37</td>
<td>1.98</td>
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<tr>
<td>$\text{La-BTC}$</td>
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<td>9.16</td>
<td>23.008</td>
<td>1.317</td>
<td>1.734</td>
<td>13.26</td>
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Table 1. Powdery Properties and Elemental Compositions of Synthesized MOFs
the experiment with standard La(OH)₃ with 2.3 mM AsO₄³⁻ and lanthanum arsenate as a final product, as shown in later parts. After the pH experiments, the supernatant was analyzed to determine the lanthanum concentration in ICP-OES. The results indicated that at pH 2, the lanthanum release was high due to the dissolution of lanthanum, which is represented in Figure 7b.

**Adsorption Kinetics.** To investigate the adsorption behavior of 2.3 mM AsO₄³⁻ on La-BA, La-BDC, and La-BTC MOFs, the kinetic study was carried out under the fixed adsorbent dose of 1 g/L. As time increases, the adsorption densities were increased and reached equilibrium within 30 min with La-BA and 360 min with La-BDC MOF. However, the La-BTC MOF showed the lowest adsorption capacity of the adsorbents due to less availability of the active sites, which is supported by the previous result by Zhang et al. for phosphate adsorption. The maximum adsorption capacities of AsO₄³⁻ on La-BA, La-BDC, and La-BTC were 2.068, 2.234, and 0.280 mmol/g, respectively, as shown in Figure 8a. The As/La atomic ratios of As/La of La-BA, La-BDC, and La-BTC were different from each other as shown in Figure 8b, where the La concentration was analyzed by ICP-OES by acid treatment.

Figure 6. XP-spectra of the La-BDC: (a) wide scan, (b) C 1s, (c) O 1s, (d) La 3d regions.

Figure 7. (a) Effect of pH. Experimental conditions: [AsO₄³⁻]₀ 2.4 mM; dose ratio 1 g/L; agitation speed 100 rpm; and temp. 25 °C and (b) residual ion concentration on AsO₄³⁻ adsorption.
decomposition. The La-BDC had a higher As/La atomic ratio of 1.98 than La-BA (0.7) and La-BTC (0.16) in which the La-BDC has a higher amount of active functional groups responsible for the adsorption of arsenate, as shown in Figure 8b. To identify the rate of $\text{AsO}_4^{3-}$ adsorption onto the La-BA and La-BDC MOFs, the pseudo-second-order kinetic model\cite{31} was applied (Figure 8c). The experimental $\text{AsO}_4^{3-}$ adsorption capacity values of ($q_{\text{exp}}$) 2.068 and 2.234 mmol/g and the calculated adsorption capacity values ($q_{\text{cal}}$) of 2.067 and 2.233 mmol/g were reasonably consistent with the observed ones for La-BA and La-BDC MOF, indicating the suitability of the pseudo-second-order kinetics model. The higher value of the rate constants ($k_2 = 2.4608 \text{ g \cdot mg}^{-1} \text{ \cdot min}^{-1}$) than the other rate constants suggested that the adsorption of $\text{AsO}_4^{3-}$ was notably faster for La-BA than the other two MOFs as shown in Table 2.

![Figure 8](image_url) (a) Effect of contact time, (b) As/La atomic ratio for La-BA, La-BDC, and La-BTC, and (c) pseudo-second-order kinetic model. Experimental conditions: $[\text{AsO}_4^{3-}]_0$ 2.4 mM; dose ratio 1 g/L; agitation speed 100 rpm; and temp. 25 °C.

Table 2. Calculated Pseudo-Second-Order Kinetic Parameters for the Adsorption of $\text{AsO}_4^{3-}$

<table>
<thead>
<tr>
<th>Materials</th>
<th>$Q_{\text{exp}}$ (mmol/g)</th>
<th>$Q_{\text{cal}}$ (mmol/g)</th>
<th>$k_2$ (g/ mmol-min)</th>
<th>$R^2$</th>
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<tr>
<td>La-BA</td>
<td>2.0676</td>
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<tr>
<td>La-BTC</td>
<td>0.2810</td>
<td>0.2885</td>
<td>0.7269</td>
<td>1.000</td>
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</table>

**Influence of Foreign Ions and NOM on the Removal of $\text{AsO}_4^{3-}$**: Naturally, ground waters and industrial effluents contain major anions, viz., chloride, sulfate, carbonate, nitrate, phosphate, silicate, and bicarbonate, which can interfere with the uptake of $\text{AsO}_4^{3-}$ by competing for surface binding sites available on lanthanum. The adsorption density of 2.3 mM $\text{AsO}_4^{3-}$ on both La-BA and La-BDC was not influenced by any other anions, except phosphate and silicate, although their initial concentration was 1 mM (Figure 9). In addition, the presence of other coexisting natural organic matters (NOM), such as humic acid (HumA), fulvic acid (FulvA), and oxalic acid (OxA), was examined. The effect of NOM interaction with $\text{AsO}_4^{3-}$ is stronger than the inorganic coexisting anions. The HumA has influenced much the adsorption of $\text{AsO}_4^{3-}$ than Fulv A due to their particle size being closer to the oxide surface, which leads to stronger repulsion. Similar behavior has also been observed by Weng et al.\cite{32,33} In addition, as discussed by our previous study\cite{34} that OxA would tend to form a complex with lanthanum leads to form a La-oxalate which blocks the active sites for adsorption of $\text{AsO}_4^{3-}$. Though the interference is high in the case of NOM for $\text{AsO}_4^{3-}$ adsorption, still the La-BDC MOF maintained its adsorption density toward $\text{AsO}_4^{3-}$. Hence, it can be concluded that these adsorbents could be utilized in real water systems.

![Figure 9](image_url) Effect of foreign ions on $\text{AsO}_4^{3-}$ adsorption. Experimental conditions: $[\text{AsO}_4^{3-}]_0$ 2.4 mM; coanion 1 mM; dose ratio 1 g/L; agitation speed 100 rpm; and temp. 25 °C.
Langmuir Isotherm: The Langmuir adsorption isotherm model\textsuperscript{35} used to identify the relationship between the equilibrium concentration ($C_e$) and the amount of $\text{AsO}_4^{3−}$ adsorbed on La-BA and La-BDC at contact temperature, 25 °C, is shown in Figure 10. The calculated maximum adsorption density ($q_m$) from the Langmuir model has a higher value than that of the other material, which corresponds to the observed data. The applicability of the Langmuir isotherm model suggests that the adsorption of $\text{AsO}_4^{3−}$ on the surface of the material is probably due to the monolayer surface complexation with La–OH moieties. The obtained $q_m$ values were also compared with the existing reports in the literature and found that the La-BDC adsorbent showed superior performance toward the removal of $\text{AsO}_4^{3−}$, which indicates that the La-BDC adsorbent can effectively remove $\text{AsO}_4^{3−}$ from water. It is noteworthy to mention that La-BDC adsorbent is one of the highest $\text{AsO}_4^{3−}$ uptake performance materials in the literature.

Reusability of the Adsorbents. The reusability of the $\text{AsO}_4^{3−}$ adsorbed La-BDC MOF was carried out to identify the cost-effectiveness and the stability of the material by successive adsorption–desorption cycles. After regeneration of each cycle with the initial concentration of 2 mM at pH 6.3 for 24 h, the adsorbent was separated, washed with 0.1 M NaOH, and freeze-dried and the freshly prepared 2 mM $\text{AsO}_4^{3−}$ was added before each run. When increasing the reuse cycle, the $\text{AsO}_4^{3−}$ adsorption densities became weak. Four adsorption and desorption cycles were carried out totally, and interestingly, the $\text{AsO}_4^{3−}$ adsorption densities were retained up to three cycles with the difference in negligible amount of material loss (Figure S1). After the fourth cycle, the interaction between $\text{AsO}_4^{3−}$ and the MOF became weak due to less active sites for adsorption as well as material loss. Also, the PXRD patterns after each cycle were carried out support the regeneration studies as the fourth cycle was complete precipitation as shown in Figure S2. These results indicated that it could be easily recovered with 0.1 M NaOH and also showed that La-BDC MOF adsorbent has sufficient chemical stability, further exhibiting favorable reuse performance over four repeated cycles.

Mechanism of $\text{AsO}_4^{3−}$ Adsorption. The mechanism of $\text{AsO}_4^{3−}$ adsorption on La-BA, La-BDC, and La-BTC is proposed as follows: the ligand of BA approached La metal, forming lanthanum methanoate instead of La-BA MOF through an acid catalyst amide-hydrolysis mechanism, confirmed by the PXRD patterns. In the La-BA structure, the formic acid acted as a good leaving group during the adsorption of $\text{AsO}_4^{3−}$. The PXRD pattern of $\text{AsO}_4^{3−}$ adsorbed on La-BA revealed the formation of lanthanum arsenate structure, supported with the standard LaAsO$_4$ PXRD pattern (JCPDS file no: 01-076-4590). From the adsorption studies, it could be concluded that the pristine As/La molar ratio was 1:0.7, which means that the remaining formate molecules were dissolved from the structure and reprecipitated with arsenate, which was also confirmed by TOC analysis. The adsorption mechanism is mainly followed by ligand exchange and the precipitation reaction. The ratio of La:As is 1:0.7, and the equilibrium pH becomes acidic, confirming the formation of the lanthanum arsenate as the final precipitated product, as shown in Scheme 2.

In the case of La-BDC, the central metal La atom has 9-fold coordination in which three oxygen atoms from hydroxyl groups and six oxygen from the BDC moiety form a distorted dodecahedron.\textsuperscript{36} According to Zhang et al.,\textsuperscript{15} the BDC prefers to complex with La through three BDC anions through the

#### Scheme 2. Possible Mechanism of $\text{AsO}_4^{3−}$ Adsorption Using La-BA

Figure 10. Langmuir adsorption isotherm of $\text{AsO}_4^{3−}$ on La-BA (red color) and La-BDC MOF (blue color). Experimental conditions: dose ratio 1 g/L; agitation 100 rpm; and temp. 25 °C.
possible linkage of a La−O−La bridge and a C−O−La interaction between BDC linker and La metal and the free hydroxyl groups are responsible for the AsO$_4^{3-}$ adsorption. The arsenate species such as H$_3$AsO$_4$ is categorized as a hard acid which tends to form a complex with hydroxyl groups of the La-cluster. The release of H$^+$ ions and the hydroxyl ions formed water to maintain a charge balance in the solution. Another possibility for the existing adsorption site is the La−O−C complex between −COOH of BDC and La, where the adsorption takes place by replacing of BDC ligand by AsO$_4^{3-}$ through a ligand exchange mechanism in which the La-BDC framework partially disintegrates the crystal structure of the La-BDC adsorbent. The partial collapse of the La-BDC structure was due to the fact that arsenate interacted with the lanthanum to form the LaAsO$_4$ precipitate. The molar ratio of La:As was 1:2, the La-BDC would tend to follow the ligand exchange rather than partial dissolution, and their chemical equilibria are different (Scheme 3). A small amount of BDC tends to be released from the structure to form lanthanum arsenate. The lanthanum−ligand interaction became weakened when AsO$_4^{3-}$ approached the metal center, which in turn caused collapse of the MOF structure by releasing the BDC groups that were dissolved and reprecipitated using the H$^+$ ions in the water. LaAsO$_4$ was confirmed by the corresponding PXRD diffractograms. Recently, Jian et al. demonstrated ZIF-8 (Zeolitic imidazolate framework-8) nanosorbent for AsO$_4^{3-}$ adsorption, and the adsorbent was not stable at acidic pH conditions, in which the metal, Zn$^{2+}$ ions were released from the structure. However, the AsO$_4^{3-}$ adsorption density on La-BDC did not affect much neutral and basic conditions as like ZIF-8. On the other hand, the La-BTC molecule has shown a considerably lower AsO$_4^{3-}$ adsorption capacity of 0.2810 mmol/g. In the La-BTC MOF, the La sites were completely occupied by the three carboxylic groups of BTC through a complex reaction. Hence, no active sites were available for AsO$_4^{3-}$ binding. In addition, it is very difficult to replace the BTC groups in La-BDC MOF with AsO$_4^{3-}$ by ligand exchange mechanism/dissolution reprecipitation, as it is a highly stable moiety as well as being most likely linked in a bidentate manner.

Characterization of Solid Residues after the Adsorption of AsO$_4^{3-}$. After the adsorption of 2.4 mM AsO$_4^{3-}$ on La-BDC (Figure 11a), the FTIR peak at 3439 cm$^{-1}$ is assigned to the −OH stretching vibration mode. The peaks at 2972 and 2824 cm$^{-1}$ were attributed to the −CH and −CH$_2$ stretching vibration mode. Also, in the green-colored La-BDC MOF, a few miscellaneous weak peaks were present. This once again confirms the presence of the BDC moiety over LaAsO$_4$. Wang et al. have already reported the release of BDC molecules during the interaction of AsO$_4^{3-}$ ions in aqueous solution. The asymmetric and symmetric vibration modes of C−O at the peak positions of 1538 and 1418 cm$^{-1}$ confirm the carboxylic groups present from the BDC moiety. The peak at 729 cm$^{-1}$ corresponds to the C−H bending vibrations of benzene. After adsorption, a new wide peak positioned at 854 cm$^{-1}$ is assigned to the −OH stretching vibration mode. The peaks at 2972 and 2824 cm$^{-1}$ were attributed to the −CH and −CH$_2$ stretching vibration mode. Also, in the green-colored La-BDC MOF, a few miscellaneous weak peaks were present. This once again confirms the presence of the BDC moiety over LaAsO$_4$. Wang et al. have already reported the release of BDC molecules during the interaction of AsO$_4^{3-}$ ions in aqueous solution. The asymmetric and symmetric vibration modes of C−O at the peak positions of 1538 and 1418 cm$^{-1}$ confirm the carboxylic groups present from the BDC moiety. The peak at 729 cm$^{-1}$ corresponds to the C−H bending vibrations of benzene. After adsorption, a new wide peak positioned at 854 cm$^{-1}$ is assigned to the stretching vibration mode of As−O−La groups, indicating that AsO$_4^{3-}$ is coordinated with La-BDC MOF. A strong band appears at approximately 447 cm$^{-1}$, which is due to the stretching vibration mode of La−O. After the adsorption of 2.4 mM AsO$_4^{3-}$ on lanthanum-methanoate, the strong and wide peak at 854 cm$^{-1}$ was attributed to the presence of La−O−As, where the methanoate molecules were...
replaced by AsO$_4^{3−}$ ions, and it formed lanthanum arsenate as a stable final product, confirmed by the PXRD pattern (JCPDS: 01-076-4590). In addition, it has been confirmed that only partial dissolution of formic acid and the BDC moiety by AsO$_4^{3−}$ occurs. The release of BDC by reprecipitating over LaAsO$_4$ was noted (Figure 11b), which showed that the less stable structure of La-BA and the MOF structure of La-BDC withstood the same reaction. The SEM images after adsorption of AsO$_4^{3−}$ on La-BA and La-BDC are shown in Figures 11c and 11d, respectively. It is worth noting that AsO$_4^{3−}$ occupied the edges on La-BA and formed an urchin-like structure of lanthanum arsenate. The AsO$_4^{3−}$ sorbed La-BDC forms a thread-like continuous structure. When compared with the structure before adsorption, the structure was not collapsed much, which confirms the stability of the MOF.

To understand the AsO$_4^{3−}$ adsorption mechanism on La-BA and La-BDC, surface compositions and surface molar ratio were further investigated by XPS. The narrow scan for the As 3d spectrum of both AsO$_4^{3−}$ adsorbed La-BA and La-BDC showed the respective characteristic peaks for E$_b$ [As 3d] at 44.3 and 44.9 eV (Figure 11e–f). This confirmed the formation of the AsO$_4^{3−}$ complex with the La-BA and La-BDC MOF. The intensity of the As 3d peak in La-BA is much higher than La-BDC, which clearly indicated the precipitation of

Figure 11. (a) FTIR spectra, (b) PXRD patterns (c–d) SEM images, and (e–f) XP spectra of La-BA and La-BDC after adsorption of 2.4 mM AsO$_4^{3−}$. 

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LaAsO₄₉ where E₀[As 3d] is close to KH₂AsO₄. On the other hand, As 3d mostly follows ligand exchange rather than chemical precipitation; hence, the intensity is very low. Further, the surface molar ratio of nAs/nLa on La-BA and La-BDC MOF after adsorption of 2.3 mM AsO₄⁻³⁻ was calculated by the XPS relative surface sensitivity factor and the results of nAs/nLa are 0.612 and 1.994 for La-BA and La-BDC, respectively, which are close to 0.70 and 1.98 obtained experimentally. The wide spectrum and the other spectrum of C 1s, O 1s, and La 3d for La-BA and La-BDC after adsorption of 2.4 mM AsO₄⁻³⁻ are shown in Figures S3 and S4.

**CONCLUSIONS**

Three types of carboxylate functionalized La-based products, namely, La-BA, La-(1,4-BDC) MOF, and La(1,3,5-BTC) MOF were successfully synthesized and characterized well before and after adsorption of high concentration (2.4 mM) of AsO₄⁻³⁻ from aqueous solution. We have successfully derived the mechanism for the formation of La-BA as lanthanum-methanoate, and La-BDC and La-BTC were identified as MOFs using standard PXRD patterns. This is the first report of an investigation of the formation of La(HCOO)₃ and the associated AsO₄⁻³⁻ uptake performance. The maximum adsorption capacities of AsO₄⁻³⁻ on La-BA and La-BDC were 0.691 and 1.936 mmol/mmol-La, respectively, which is one of the highest AsO₄⁻³⁻ uptake capacities compared to many previously reported materials to date. The adsorption density of AsO₄⁻³⁻ on both La-BA and La-BDC was not influenced by any other anions, except phosphate and silicate although the initial concentrations of both AsO₄⁻³⁻ and interfering anions are equimolar. The AsO₄⁻³⁻ adsorption capacity on both La-BA and La-BDC did not have obvious differences over the wide pH range of 3–11 and remained constant. The FTIR spectra suggest the formation of the As−O bond with peaks at 854 cm⁻¹ for La-BA and La-BDC, and PXRD patterns confirm the formation of LaAsO₄ along with the MOF moieties after adsorption. The XPS-spectra also confirmed that the characteristic E₀ peaks at 44.3 and 44.9 eV were corresponding to As⁺−O on La-BA and La-BDC, respectively. The mechanism of AsO₄⁻³⁻ adsorption by La-BA mainly occurs by ligand-exchange followed by chemical precipitation. On the other hand, La-BDC mainly features ligand-exchange. The adsorption of AsO₄⁻³⁻ onto carbonate-mediated La-based adsorbents follows pseudo-second-order kinetics, suggesting that the adsorption of AsO₄⁻³⁻ on the adsorbents might involve chemisorption. These results suggest that La-BA and La-BDC MOF are superior materials to remove AsO₄⁻³⁻ from waters.

**ASSOCIATED CONTENT**

*Supporting Information* The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b06489.

XP-spectra of the AsO₄⁻³⁻ adsorbed La-BA and La-BDC: (a) Wide scan (b) C 1s spectrum, (c) O 1s spectrum, and (d) La 3d spectrum (Figure S1 and Figure S2), regeneration study (Figure S3), PXRD patterns of the La-BDC after each regeneration cycle (Figure S4), a comparison table with the reported materials in the literature (Table S1), adsorption characterization techniques, and the equations of the pseudo-second-order kinetic model and Langmuir adsorption isotherm (PDF).

**AUTHOR INFORMATION**

*Corresponding Author*
*Prof. Keiko Sasaki: Tel & Fax: +8192 802 3338. E-mail: keikos@mine.kyushu-u.ac.jp.*

**ORCID**
Subbaiah Muthu Prabhu: 0000-0003-1553-3136
Keiko Sasaki: 0000-0002-2882-0700

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**REFERENCES**


