

Direct Arsenic Removal from Water Using Non-Membrane, Low Temperature Directional Solvent Extraction

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Abstract

Arsenic (*As*) poisoning in water due to natural minerals or industrial pollution is a critical global problem that threatens the health and life of billions. Current arsenic removal techniques involving chemical reaction, ion exchange, or membrane processes can be expensive, inaccessible or infeasible for underdeveloped regions or remote areas. Here, we demonstrate that using a so-called directional solvent extraction (DSE) process, arsenic ions in water can be effectively removed without the need of a membrane or chemical reaction, and this process promises to utilize very low temperature heat (as low as 45 °C). We have tested feed water with different arsenic concentrations and arsenic ions in different forms (*As*-III and *As*-V) commonly found in nature. It is demonstrated that DSE using decanoic acid as the directional solvent can purify contaminated water to meet the drinking water standard (arsenic concentration < 10 parts per billion, ppb), and the arsenic removal efficiencies are higher than 91% for *As*-III and 97% for *As*-V. Moreover, DSE can remove *As*-III directly without the need of pre-oxidation, which is required in most of the state of art techniques. DSE can potentially lead to effective arsenic removal technologies with low resource settings that are suitable for remote and underdeveloped regions, which are impacted by arsenic poisoning the most.

1. Introduction

Heavy metal pollution in water endangers the health and life of billions of people in the world. For example, arsenic (*As*) pollution in Bangladesh has led to chronic poisoning of tens of millions¹⁻³ and is found responsible for 20% of the death in the area.⁴ Such problems are not unique to underdeveloped countries but also exist in developed ones like the U.S. It is reported⁵ that the concentration of arsenic in the water from California natural water resource is higher than the U.S. Environmental Protection Agency's (EPA) standard of 10 ppb (parts per billion).⁶ The major source of arsenic pollution is natural mineral release into the underground water,⁷ but human activities such as mining have also caused significant arsenic pollutions. The concentration in naturally arsenic-polluted water ranges from 10 – 3100 ppb,⁸ while that in industrial polluted water can reach even much higher values.⁹

Excessive arsenic exposure can lead to significant short and long-term health problems, such as neurologic and immunologic defects.^{10, 11} It is especially harmful to children as it can be detrimental to their central nervous system and cognitive development.^{10, 11} There are more than 20 different arsenic compounds identified in nature,¹² but the major concerns are from arsenite (*As*-III) and arsenate (*As*-V). *As*-III binds to sulfhydryl groups, impairing the function of many proteins, while *As*-V inhibits oxidative phosphorylation, thereby short-circuiting life's main energy generation system.¹³ In the U.S., the new arsenic maximum contaminant level (MCL) will require the addition of arsenic treatment technologies to many community water supplies. The EPA has listed only Point-of-use (POU) reverse osmosis, POU activated alumina and point-of-entry (POE) activated alumina as viable treatment technologies. All the currently known technologies suitable for POU, POE¹⁴ and small community treatment systems are less effective in removing *As*-III compared to *As*-V,¹⁵ which is the natural form of arsenic in many water supplies. At pH of 6.5-8.5, *As*-III is less polar than *As*-V which is usually present in the form of singly and doubly charged $H_2AsO_4^-$ and $HAsO_4^{2-}$ anions in oxidizing water.¹⁵ As a result, processes that remove anions (e.g., anion exchange and activated alumina adsorption) can be used for removing *As*-V but less effective for *As*-III. Other small scale processes that are suitable for removing *As*-V anions include iron coagulation followed by multimedia filtration or microfiltration.¹⁵ Iron oxide-based adsorbents⁹ such as granular ferric hydroxide (GFH) and iron-doped filtration as well as adsorption media have been used. In general, adsorbent-based methods work by chemical reaction between arsenic compound and adsorbents. They will reduce the concentration of arsenic in water, but are usually not able to produce drinkable water quality (<10 ppb *As*) directly. It has also been pointed out that the practical use of conventional adsorbent techniques is still limited due to their low adsorption capacities and the lack of means to regenerate and reuse the adsorbents.¹⁶ There has also been novel techniques using nanomaterials made of carbon, titanium, iron, ceria, or zirconium for arsenic removal. But their high surface energies usually lead to aggregate, reducing their capability, lifetime and potential for real life application.¹⁶

Other methods like electrodialysis will remove *As*-V but cannot remove any *As*-III.¹⁷ Reverse osmosis and nanofiltration¹⁸⁻²⁶ can also be used for arsenic removal but generally does a better job in removing *As*-V compared to *As*-III.²⁷ Even with double filtration using reverse osmosis membranes, the *As*-III removal efficiency is at most 95%.²⁸ In addition, the required pressure in reverse osmosis is high, and this method needs high quality membranes which require regular maintenance.²⁹ After examining all these treatment possibilities, it is apparent that *As*-III removal is much more challenging, and as a result it must be oxidized to *As*-V for effective removal,^{17, 27} which may be achieved by chlorine,

permanganate, ozone and manganese-oxide-based solid media.¹⁵ Membrane distillation has also been used for water purification including removing arsenic.³⁰⁻³⁵ Leveraging thermal evaporation – a physical method – membrane distillation is effective for both *As*-III and *As*-V removal. When a high vacuum is applied, it can utilize relative low temperature heat sources,³³ but maintaining a vacuum may hinder its application in low-resource settings and POU applications, and it still needs membranes.

Using solvent extraction for water treatment has been studied for decades. It was first explored by Davison and coworkers in the 1950s.³⁶ However, these methods were discontinued due to significant solvent residue in the produced water.³⁷ Recently, a much improved solvent extraction method, called directional solvent extraction (DSE), has been demonstrated to extract water from saline sources while leaving almost no residue in the produced water.³⁸⁻⁴⁰ The directional solvents used were decanoic acid and octanoic acid, which are important ingredients in many dairy products. For example, decanoic acid exists in whole milk with a concentration of 1300 ppm (parts per million).⁴¹ The name “directional solvent” was coined because it is insoluble in water but can dissolve some water, and reject salts. The water solubility in the solvent increases with temperature, allowing it to extract fresh water at an increased temperature and release it at a lower temperature. Such a DSE process was proven effective with a top temperature as low as 40 °C,⁴⁰ making it suitable to utilize low grade heat like waste heat or direct solar heating.

The DSE process has been proven effective in removing ions from seawater (3.5% wt%) and even water with very high salinities (~30 wt%).^{40, 42, 43} The recovered water from simulated seawater was initially < 700 ppm,⁴⁰ and improved protocol has shown that the recovered water can meet the drinking water standard of < 500 ppm.⁴³ However, arsenic pollution is usually at much lower concentrations than the salts dissolved in seawater, and the safety limit of 10 ppb is also at a completely different level than common salts due to the high toxicity. Despite some differences among different countries, the safety levels of arsenic are all stringent. For example, Europe and the U.S. have a standard of 10 ppb, while many other countries such as Bangladesh set this threshold to 50 ppb.

In this work, we combine molecular simulations and experiments to demonstrate the use of directional solvents to remove arsenic ions from contaminated water without the need of a membrane or chemical reaction. This solvent can extract fresh water from arsenic-contaminated water sources and release the fresh water by a temperature difference. Using decanoic acid as the directional solvent, this technique can remove both *As*-III and *As*-V ions directly without the need of pre-oxidizing *As*-III and produce fresh water meeting the drinking water standard (<10 ppb *As*). We also show that the DSE method can be effective at a temperature as low as 45 °C, leading to the possibility of using low temperature sources such as waste heat from industrial and residential processes or solar heating. These advantages make DSE a promising alternative to existing membrane- and chemical-based methods for arsenic removal. The low-resource setting feature of DSE also makes it a perfect technique for underdeveloped and remote regions.

2. Results and Discussion

2.1. Molecular level mechanism of DSE for Arsenic removal

In this work, we study DSE with both octanoic acid and decanoic acid as directional solvents, both are fatty acids. In general, some fatty acids dissolve water due to the presence of the carboxylic acid group

(-COOH). The highly polar C=O and O-H groups form hydrogen bonds with water molecules (Fig. 1a). While this end of the molecule is hydrophilic, the rest of the fatty acid molecule consisting of CH₂ and CH₃ segments is hydrophobic. Fatty acids with very small chain lengths are miscible with water because the interaction between the hydrophilic head group and water dominates. However, as the chain length increases, the solubility of both substances in each other decreases due to the more pronounced effect of the hydrophobic alkyl backbone. Octanoic acid and decanoic acid are two fatty acids tested to have the “directionality” in solubilities. When using decanoic acid as the directional solvent, the residual concentration in the product water is measured to be 36 ppm⁴⁰ with a theoretical prediction of 28 ppm.³⁸ This concentration is much smaller than that in many dairy products (> 1000 ppm).⁴¹ Octanoic acid can have higher residual concentration in product water since its solubility in water is 680 ppm.⁴⁴ As a comparison, the concentration of octanoic acid in milk is 565 ppm.⁴¹ Despite this drawback, we still choose to study the ability of octanoic acid in DSE treatment of arsenic water as a comparison to decanoic acid.

We first use molecular dynamics (MD) simulations to evaluate the possibility of arsenic ion removal using decanoic acid and octanoic acid. Both *As*-III (*As*(OH)₃) and *As*-V (*H*₂*AsO*₄⁻) compounds are studied. The arsenous acid is simulated here for *As*-III since it is a weak acid with pK_a=9.2, which resembles the conditions in natural water better.⁴⁵ MD simulations are combined with thermodynamic integration to calculate the solvation free energies of different arsenic ions in directional solvents, which are then compared to those in water. In brief, arsenic ions are simulated to “gradually appear” into the solution, and free energy needed for this process is calculated as the free energy of solvation (Fig. 1b). By comparing the solvation free energies, we can determine in which environment the arsenic ions are more thermodynamically stable, which will help evaluate if arsenic removal using DSE is possible. The details of MD simulations and thermodynamic integration can be found in the Methods section.

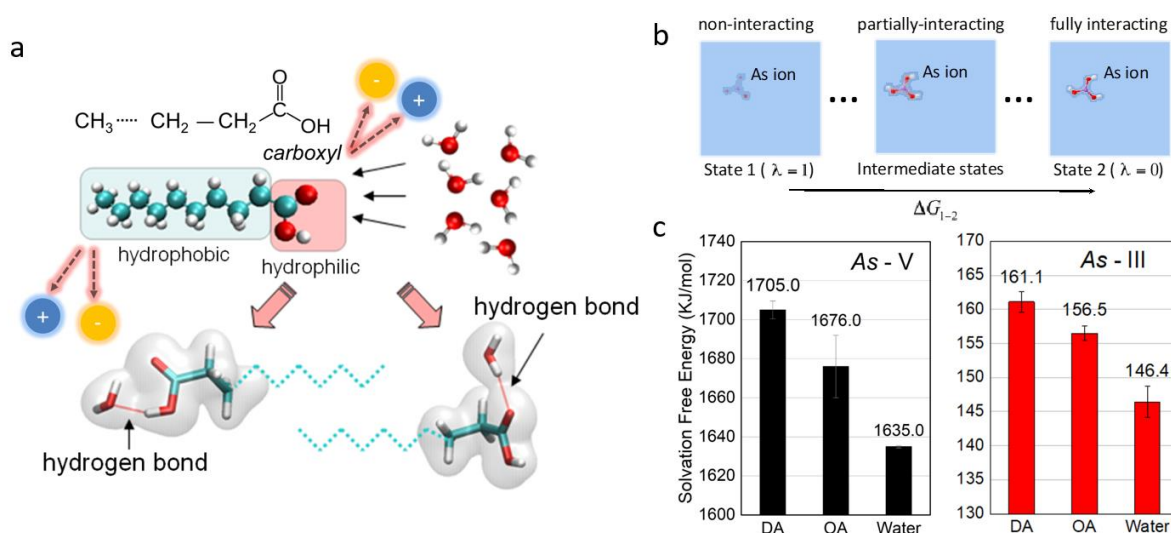


Figure 1. (a) Schematic of the mechanism of directional solubility characteristics of fatty acids. The subtle balance between the hydrophilic head and hydrophobic tail of the fatty acid molecules allows the absorption of water molecules due to hydrogen bonding while keep themselves from being dissolved in water, and in the meantime, they reject salt ions. (b) Schematics of “gradually appearing” an arsenic ion in a solvent for calculating the free energy difference using MD simulations and thermodynamic integration. Here, λ is a coupling factor that tunes the interatomic interactions between the ion and solvent, with $\lambda = 1$ corresponding to the non-interactions state

and $\lambda = 0$ corresponding to the fully interacting states. (c) Solvation free energies of *As*-III ($As(OH)_3$) and *As*-V ($H_2AsO_4^-$) in decanoic acid (DA), octanoic acid (OA) and water.

The calculated free energies of *As*-III and *As*-V are summarized in Fig. 1c. The results show that both *As*-III and *As*-V ions have lower free energies when dissolved in water than in the two directional solvents. This suggests that arsenic ions are more thermodynamically stable in the water phase than in the solvents. Between decanoic acid and water, the differences in free energies for *As*-III and *As*-V are respectively 14.7 kJ/mol and 70.0 kJ/mol, which are large free energy barriers to prevent arsenic ions from diffusing into decanoic acid from water. This means that these arsenic ions can be rejected effectively by decanoic acid in the DSE process. For octanoic acid and water, the same observations are made, and the differences in free energies are 10.1 kJ/mol for *As*-III and 41.0 kJ/mol for *As*-V. These energy barriers are respectively smaller than their counterparts when decanoic acid is used as the solvent, but they should still be sufficiently large to prevent arsenic ions from diffusing from water to octanoic acid.

2.2. DSE Experiments

To experimentally demonstrate the arsenic removal, simulated *As*-III and *As*-V containing feed water with concentrations ranging mainly from ~40 ppb to 400 ppb are prepared (see Methods section). These concentrations are chosen to match the most common range of the arsenic content in natural water,^{46, 47} which present most widespread risk for drinking water-induced arsenic poisoning. The DSE experimental procedure is briefly depicted in Fig. 2: (a) 300 mL of decanoic acid ($CH_3(CH_2)_8COOH$, $\geq 98\%$, Sigma-Aldrich) mixed with 150 mL of arsenic water are placed in a 600 mL beaker; (b) The content in the beaker, which is capped to prevent evaporation, is heated to a higher temperature (85 °C, 55 °C or 45 °C) and stirred for fully mixing; (c) The mixture is then held at the high temperature in a water bath, allowing the arsenic water to settle to the bottom of the beaker; (d) The top layer, which is the decanoic acid with pure water dissolved in it, is then transferred to several clean 50 mL plastic tubes; (e) The test tubes are then placed in a lower temperature water bath at 35 °C, allowing the dissolved water to precipitate out of the solution due to lower solubility at reduced temperatures; (f) Precipitated water settles to the bottom of the test tubes and is decanted to measure the concentration of arsenic in the recovered water. All steps are given excess time to ensure that equilibrium is reached, but this process can be speeded up if using a large scale continuous process.^{42, 48, 49} The above procedure is repeated for experiments with octanoic acid ($CH_3(CH_2)_6COOH$, $\geq 98\%$, Sigma-Aldrich) as the solvent, expect that the lower temperature is set to 24 °C.

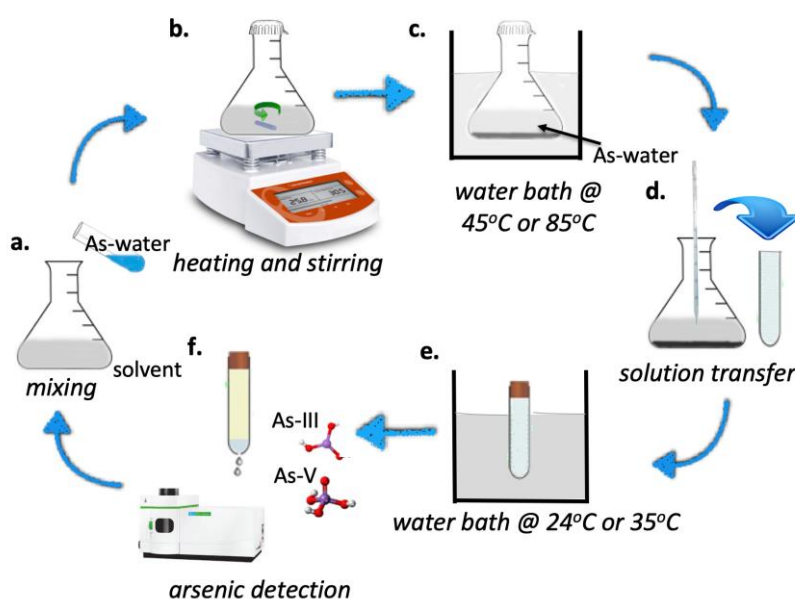
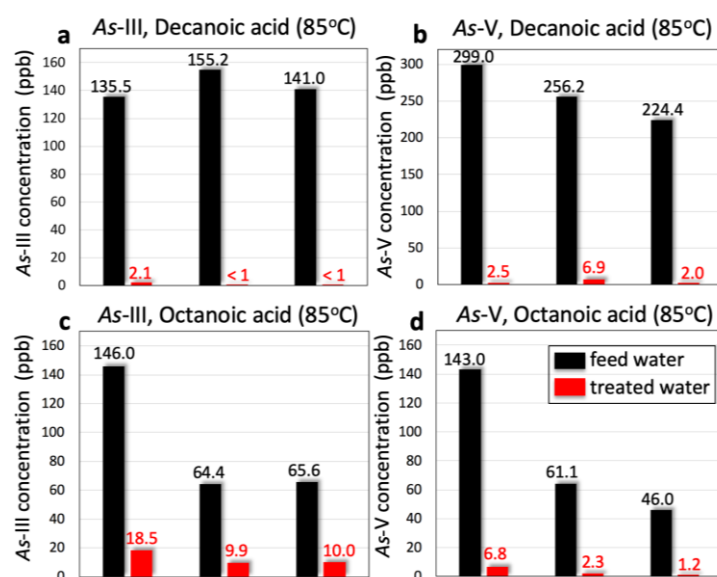


Figure 2. DSE experimental process for arsenic removal.

The measured arsenic concentrations in the DSE-treated water together with the feed water concentrations are shown in Fig. 3 for different top process temperatures (85 °C, 55 °C or 45 °C). The data from the top process temperature of 85 °C (Figs. 3a-d) indicate that decanoic acid can effectively remove almost all *As*-III and *As*-V ions in all cases tested. For *As*-III, the feed water contains arsenic in the range of 135-155 ppb, which are higher than most naturally contaminated water. For these cases, the DSE-treated water contains no more than 2.1 ppb of arsenic, with two cases showing no detectable level of arsenic (Fig. 3a). We note that our machine has a detection limit of 1 ppb. These values are below the stringent EPA and WHO drinking water standard of 10 ppb and are far from standards in countries like Bangladesh (50 ppb). It is worth special mentioning that decanoic acid can directly eliminate *As*-III in water without the need of chemically converting it to *As*-V before purification which is almost universally needed in the state of the art arsenic removal techniques. For *As*-V (Fig. 3b), with the feed concentrations below 300 ppb, DSE can purify the water to contain less than 7 ppb arsenic, which is lower than the EPA and WHO limits.



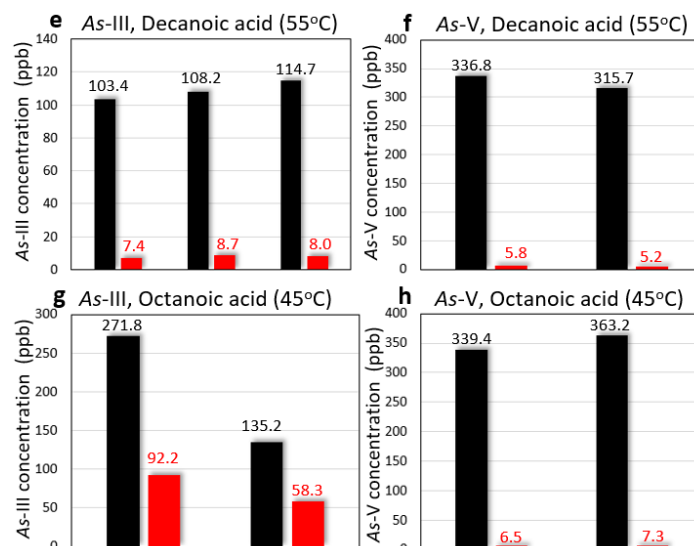


Figure 3. Arsenic concentrations of feed (black bars) and DSE-treated (red bars) water for (a) *As*-III treated using decanoic acid, (b) *As*-V treated using decanoic acid, (c) *As*-III treated using octanoic acid, (d) *As*-V treated using octanoic acid, (e) *As*-III treated using decanoic acid at low temperature, (f) *As*-V treated using decanoic acid at low temperature, (g) *As*-III treated using octanoic acid at low temperature, and (h) *As*-V treated using octanoic acid at low temperature. Note: in panel (a) the recovered water in the last two cases show non-detectable level of arsenic below the machine detection limit of 1 ppb.

With a top process temperature of 85 °C, octanoic acid as the directional solvent shows slightly inferior performance than decanoic acid. For *As*-III, when the feed water concentration is 146.0 ppb, the DSE-treated water contains 18.5 ppb arsenic (Fig. 3c). It is expected that a second DSE treatment cycle will bring down the arsenic content below the 10 ppb limit. For lower feed concentrations around 65 ppb, octanoic acid is sufficiently effective to reduce the arsenic content to ~10 ppb in one treatment. Octanoic acid shows better removal efficiency for *As*-V. As shown in Fig. 3d, water with 143.0 ppb *As*-V is purified to contain only 7 ppb of arsenic after DSE treatment. For lower feed concentrations ranging from 46-62 ppb, further lower arsenic contents (1-2 ppb) are detected in the treated water. This makes octanoic acid capable of direct *As*-V removal with a single DSE treatment cycle.

For decanoic acid, we have also performed the experiment with a top process temperature of 55 °C, and for octanoic acid, the top temperature is set to 45 °C to test the DSE performance of these two fatty acids at low temperatures. We note that for decanoic acid the lowest process temperature needs to be above its melting temperature of ~34 °C, we thus choose to use a higher top temperature for decanoic acid than octanoic acid, which is still liquid at room temperature (24 °C). For the treatment of *As*-III using decanoic acid, the feed water contains arsenic in the range of 100-115 ppb, which is similar to the common natural arsenic water concentration. The DSE-treated water contains 7.4-8.7 ppb of arsenic (Fig. 3e), meeting the drinking water standard. For *As*-V, decanoic acid is able to bring the arsenic concentration from 310-340 ppb to less than 6 ppb after treatment (Fig. 3f). For the treatment of *As*-III by octanoic acid, similar to the 85 °C cases, the results are also inferior than decanoic acid. The feed water contains arsenic in the range of 130-275 ppb, and after the treatment, the residual concentration of *As*-III remains higher than 55 ppb (Fig. 3g). For *As*-V, octanoic acid shows similar outstanding arsenic removal capability as decanoic acid (Fig. 3h).

We summarize the arsenic removal efficiencies in Table 1. It is shown that decanoic acid as the directional solvent has high arsenic removal efficiency ($> 97\%$ at high temperature and $> 91\%$ at low temperature) and can reduce the arsenic levels below the drinking water limit in one DSE cycle. Octanoic acid is effective in removing *As-V* from water with removal efficiencies greater than 95.2% . It is less effective for *As-III* removal with rates around $84.6\text{--}87.3\%$ at high temperatures and $57.0\text{--}66.0\%$ at low temperatures. One possible reason for this could be inferred from the solvation free energy barriers. As calculated from the MD simulations, it has a relatively lower energy barrier to move *As-III* ions from water to octanoic acid compared to the other three cases. Another possible reason is from the incomplete separation. In the arsenic water separation (step c in Fig. 2), we used gravity-driven spontaneous separation. There might still be some metastable small arsenic-containing water droplets suspended in the solvent, which we could not visually identify and are not fully settled down. These droplets eventually get mixed into the treated water. When the top process temperature is lowered, the amount of water that can be recovered from the same protocol is smaller, and thus the unseparated arsenic water droplets in step c of Fig. 2 may have a larger impact on the arsenic concentration of the produced water. This may explain why both fatty acids show lower performance at lower temperature than at $85\text{ }^{\circ}\text{C}$ in treating *As-III*. However, it is very possible that using other separation techniques, such as centrifuge⁴² or electrocoalescence,⁵⁰⁻⁵² to facilitate more complete separation, the arsenic residue in the recovered water can be further lowered. Nevertheless, we have proven that using decanoic acid, the DSE-treated water can meet the drinking water standard in arsenic concentrations.

Table 1. Arsenic removal efficiencies

Ion	Directional solvent	Removal efficiency at high temperature	Removal efficiency at lower temperatures
<i>As-III</i>	decanoic acid	$> 98.4\%$	$91.4\% - 93.0\%$
<i>As-V</i>	decanoic acid	$97.3\% - 99.2\%$	$98.2\% - 98.3\%$
<i>As-III</i>	octanoic acid	$84.6\% - 87.3\%$	$57.0\% - 66.0\%$
<i>As-V</i>	octanoic acid	$95.2\% - 97.8\%$	$97.9\% - 98.1\%$

In Fig. 4, we compare the arsenic removal efficiency to those of reverse osmosis, nanofiltration and membrane distillation techniques in the literature. It is seen that DSE with decanoic acid has superior *As-III* removal capability compared to reverse osmosis and nanofiltration and very similar performance as membrane distillation when operating with a top process temperature of $85\text{ }^{\circ}\text{C}$. At lower temperatures, DSE with decanoic acid is better than all but membrane distillation. We note that membrane distillation needs vacuum and membrane, while DSE is membrane-free and operates at normal conditions. DSE with octanoic acid, although not as effective as decanoic acid, is still better than most of the current methods. As expected, *As-V* can be removed more effectively than *As-III* using reverse osmosis and nanofiltration, and this is why *As-III* are usually oxidized into *As-V* for effective removal. For removing *As-V*, DSE using decanoic acid again is on a par with the best current methods, and that using octanoic acid is better than most of the current methods.

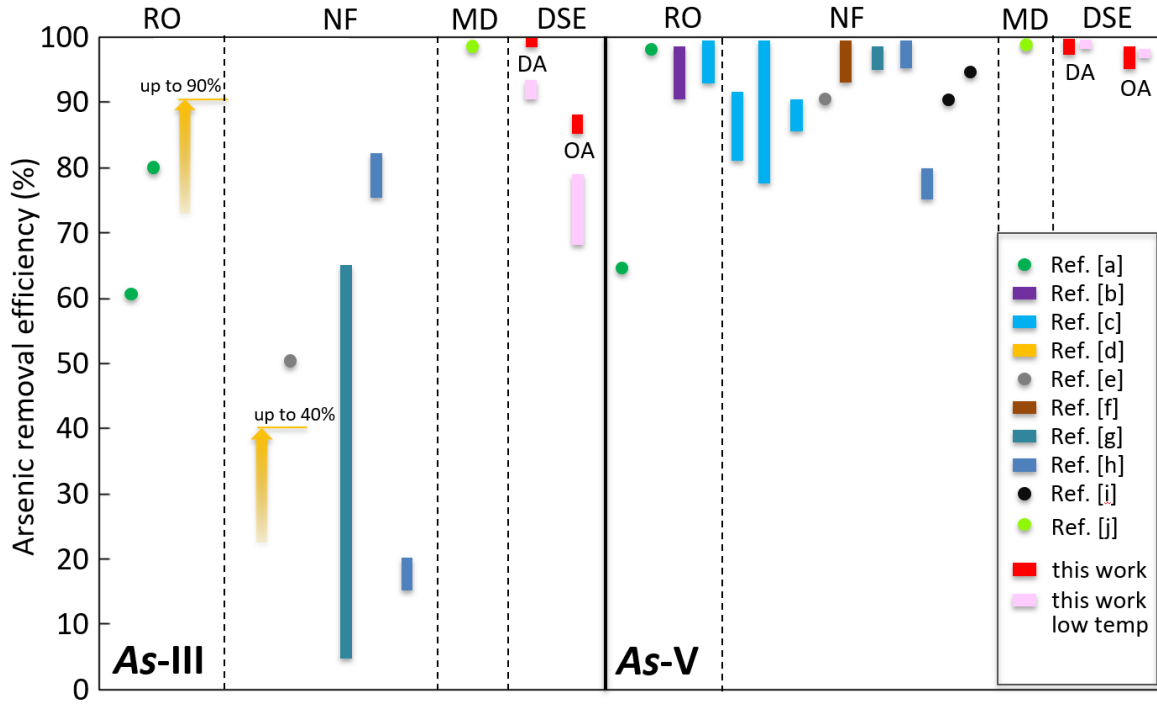


Figure 4. Comparison of DSE arsenic removal efficiency with state of the art reverse osmosis (RO) and nanofiltration (NF) methods. DSE using DA represents the best *As*-III removal technique, while the performance of DSE in *As*-V removal is on a par with the best techniques. References cited in the plot are: [a] – Ref. [20]; [b] – Ref. [18]; [c] – Ref. [23]; [d] – Ref. [21]; [e] – Ref. [24]; [f] – Ref. [25]; [g] – Ref. [26]; [h] – Ref. [19]; [i] – Ref. [22] and [j] – Ref. [30–35].

Besides the feed *As*-III and *As*-V concentrations below 400 ppb, we have also tested feed water with higher arsenic contents of ~11000 ppb *As*-III, ~1200 ppb and ~730 ppb *As*-V using decanoic acid. Such high concentration of arsenic in water can be found in some industrial fields such as the metallurgy waste water.⁹ For the 11000 ppb *As*-III water, DSE is able to reduce the arsenic concentration to ~360 ppb, corresponding to a 96.8% removal rate. For the 1200 ppb and 730 ppb *As*-V water, arsenic concentration can be reduced to 59 ppb and 22 ppb respectively, corresponding to 95% and 97% removal rates. It is expected that the arsenic contents in these two feed concentrations can be reduced to the safe limit of 10 ppb with a second round of DSE treatment.

Lastly, we emphasize that the DSE process can utilize low temperature thermal energy, which can be from sources like waste heat and solar heating. Evaluating the exergy consumption, which characterizes the maximum work extractable from the heat source at Carnot efficiency, highlights the low temperature feature of DSE. It has been estimated that the exergy consumption of the DSE process is lower than that of distillation processes when using heat with temperatures below 70 °C. DSE can also be more exergetically efficient than reverse osmosis when operating below 50 °C.⁴⁰ We further note that since DSE can use heat sources at temperature of ~45 °C, it can actually harvest heat rejected by most industrial and residential processes, which would be otherwise wasted. Besides its superior ability to remove arsenic, the possibility of DSE to tap into the enormous amount of waste heat worldwide may present a great impact to the water-energy nexus. We would also like to point out that developing more effective directional solvents with increased yields (i.e., the amount of fresh water produced by one unit

of solvent in one DSE cycle) should be a focus of future research, which can lead to further reduction in energy consumption and thus eventually treatment cost. Of course, better engineering design (e.g., heat recovery, flow optimization and etc.) will also be critical to realizing the practical development of the DSE technology.

3. Conclusions

In this work, we demonstrate that DSE, as a non-membrane and low temperature technique, can effectively remove both *As*-III and *As*-V ions from water. Our measured arsenic concentration of DSE-treated water show that decanoic acid can remove both types of ions with removal efficiencies greater than 97% when operating with a top process temperature of 85 °C. Octanoic acid as the directional solvent has similar performance for *As*-V removal, but has a lower removal efficiency for *As*-III. When operating at lower temperatures, decanoic acid can still have satisfactory efficacy in the arsenic removal. These results are backed by MD simulations, which predict that arsenic ions can be rejected by the directional solvents. For feed arsenic concentrations that is common in natural water, DSE using decanoic acid can reduce both *As*-III and *As*-V to below the EPA and WHO drinking water limit of 10 ppb with a single treatment. For *As*-V, octanoic acid can achieve the same results, while for *As*-III, DSE treatment using octanoic acid for two times will be needed. It is important to demonstrate that DSE can directly remove *As*-III without pre-oxidation, which is commonly needed for conventional techniques. The DSE technique, which can utilize low temperature heat, can potentially result in low resource setting and inexpensive arsenic removal technologies that are especially valuable for remote and underdeveloped regions, which are impacted by arsenic poisoning the most. This work is also expected to further stimulate research around the DSE technology.

Methods

Molecular dynamics simulation details

MD simulations are performed using the GROMACS (Groningen Machine for Chemical Simulations) package.⁵³ The all-atom optimized potential for liquid simulation⁵⁴ (OPLS-aa) force field is used for decanoic and octanoic acid molecules, which has shown good accuracy in free energy calculation in our previous work.³⁸ The TIP3P water model⁵⁵ is used to simulate water molecules. There are, however, no parameters for the arsenic ions of interest in the OPLS-aa force field. To resolve the problem for *As*-V ions, we take the OPLS-aa potential parameters for phosphate ions, which have the same atomic structure as *As*-V ions, and scale the bond and angle force constants respectively by 0.70 and 0.72 by comparing their density functional theory-calculated IR spectra. The As-O bond length is estimated to be 0.137 Å longer than the P-O bond length. We then build dihydrogen arsenate (*As*-V) structures according to coordinate data provided by Jmol and the National Institutes of Health.⁵⁶ To simulate *As*-III ions, the structure of *As*(OH)₃ provided by Jmol is used. In the simulations, a cutoff of 1.0 nm for van der Waals (vdW) and short-range electrostatic interactions is used. For the long range electrostatic interactions, the Fast Particle-Mesh Ewald (PME)⁵⁷ method with a 0.12 nm spacing for the fast-Fourier transformation (FFT) grid and a 6th order interpolation scheme are used. All bonds are constrained by the Parallel Linear Constraint Solver (P-LINCS),⁵⁸ and a time step of 2 fs is used for all simulations. Cubic simulation boxes with sides of ~4.1 nm are used to guarantee that there is no interaction between the ion and its images in the periodic cells. This enables the simulation of a dilute limit.

Free energy calculation

The free energy is calculated using thermodynamic integration with the coupling factor method.⁵⁹ We briefly describe the methodology and procedures of our calculations, and more detailed descriptions can be found various references such as ref.[⁵⁹]. In the coupling factor method, in order to calculate the free energy difference between two states, the Hamiltonian of a system, H , is manually changed by adjusting the coupling factor λ using the soft-core strategy.⁶⁰ The free energy difference between two states, ΔG_{1-2} , can be calculated as:

$$\Delta G_{1-2} = \int_{\lambda_1}^{\lambda_2} \left\langle \frac{\partial H(\lambda)}{\partial \lambda} \right\rangle d\lambda \quad (1)$$

where the angle bracket denotes ensemble average. In the free energy calculation using thermodynamic integration, an ion dissolution process is simulated by “appearing” the ion in the solvent through gradually switching on the non-bonded interactions, including vdW forces and electrostatic interactions, between the ions and the solvent molecules (Fig. 1b). This is done through appropriately formulating the λ -dependent non-bonded potential functions, with $\lambda = 1$ corresponding to the non-interactions state and $\lambda = 0$ corresponding to the fully interacting states. Around 50 discrete λ points are chosen between 1 and 0, and $\partial H(\lambda)/\partial \lambda$ is evaluated analytically in each MD simulation with different λ values. The details of the λ -dependent potential functions can be found in ref.[⁶⁰].

In each simulation, the system is firstly equilibrated with constant volume (NVT ensemble) for 20 ps and followed by further equilibration with constant pressure (NPT ensemble) for 100 ps. Then, a 25 ns production run in the NPT ensemble is performed, where the derivative, $\partial H(\lambda)/\partial \lambda$, is evaluated and time-averaged. After collecting all the derivatives at each λ point, trapezoidal numerical integrations are used to obtain the free energy difference using Eq. (1). In our simulations, around 50 λ points are used for each calculation. According to our tests, by adding more λ points to make the grid denser, the calculated free energy does not vary beyond the error bar. Errors are analyzed by utilizing block averaging. All simulations are performed at 350 K. To test the model and method, we calculated the free energy of NaCl in water and obtained a value of 729.8 ± 1.2 kJ/mol, which compare favorably to the literature data of ~ 728 kJ/mol in refs.[^{61, 62}].

To make a meaningful comparison between the free energies, a common reference is needed. According to definition, the solvation free energy of an ion in a solvent is the free energy different between the state when it is in the crystalline solid and the one when it is dissolved in the solvent. This process includes two steps: breaking up the lattice and dissolving the resulted gaseous ion. However, in our simulation the purpose is comparing the tendency of ions being dissolved in water versus in directional solvents, and thus the first step will be identical in all simulations. As a result, we only need to calculate the free energy change in the second step.

Arsenic feed water preparation

To simulate typical arsenic water, dihydrogen arsenite (As -III) and dihydrogen arsenate (As -V) water solutions are prepared. Sodium arsenite solution procured from Sigma-Aldrich with a concentration of 0.05 mol/L is used to prepare the As -III solution, and 98% sodium hydrogen arsenate heptahydrate from VWR is used to prepare As -V. Both are used without further

purification. These two kinds of ions are each dissolved separately in deionized water to form feed solutions with concentrations ranging from ~40 ppb to ~11000 ppb with most of them below 300 ppb. This range is chosen to match the most general range of the arsenic concentration in water.^{46, 47}

Arsenic concentration measurement

All arsenic concentration measurements are performed using Perkin Elmer Optima 8000 ICP-OES or MITERAC ICP-MS systems. A set of calibration curves of conductivity versus arsenic ion concentration are established prior to the measurements. The Perkin Elmer Optima 8000 has a detection limit of 25 ppb while the MITERAC ICP-MS systems have a detection limit down to 1 ppb. These two systems are used complementarily to cover the necessary arsenic concentration range.

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