

ARTICLE

Comparative Study Between Two Zeolitic Imidazolate Frameworks as Adsorbents for Removal of Organoarsenic, As(III) and As(V) Species from Water

Khalil Ahmad^{1,2*}✉, Habib-ur-Rehman Shah¹@, Muhammad Ahmad³ ID, Muhammad Mahboob Ahmed⁴ ID, Khalida Naseem⁵ ID, Nagina Naveed Riaz^{6,7} ID, Ali Muhammad¹, Asif Ayub¹ ID, Munir Ahmad⁷, Zahoor Ahmad⁸ ID, Alisha Munwar⁴, Abdul Rauf¹ ID, Riaz Hussain⁹ ID, Muhammad Ashfaq^{1*}✉

¹Institute of Chemistry, Baghdad ul Jadeed Campus, The Islamia University of Bahawalpur, Bahawalpur, 63100, Pakistan

²Faculty of Science, Department of Chemistry, University of Central Punjab, Bahawalpur Campus, Bahawalpur, 63100, Pakistan

³Department of Chemistry, University of Sahiwal, Punjab, 57000, Pakistan

⁴Institute of Chemical Sciences, Bahauddin Zakariya University, Multan, Pakistan

⁵Faculty of Science, Department of Chemistry, University of Central Punjab, Lahore, Pakistan

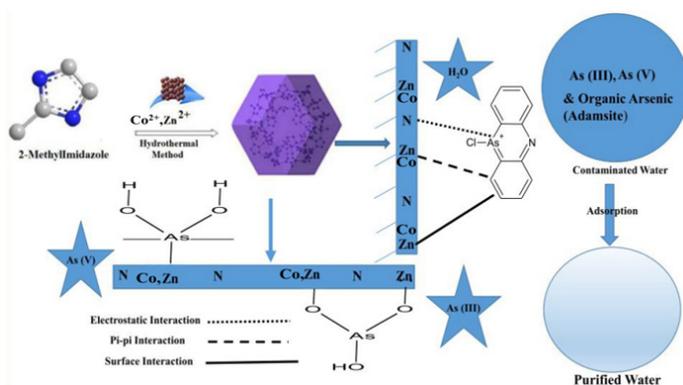
⁶Department of Chemistry, Division of Science & Technology, University of Education, Lahore, Pakistan

⁷Department of Chemistry, Khawaja Fareed University of Engineering and Technology Rahim Yar Khan, Pakistan

⁸Faculty of Science, Department of Botany, University of Central Punjab, Bahawalpur Campus, Bahawalpur, 63100, Pakistan

⁹Department of Chemistry, Division of Science & Technology, University of Education, Dera Ghazi Khan Campus, Pakistan

@ = Authors have equal contribution.



Water-stable zeolitic imidazolate frameworks (ZIF) with zinc and cobalt cations were synthesized to explore the effect of metal ions on arsenic adsorption. At room temperature (25 ± 2 °C) and pH 7.8, maximum adsorption capacities of arsenic (As^{5+}) on the surface of ZIF-8 and ZIF-67 were 87.03 and 86.70 mg g^{-1} respectively, with encouraging results up to 95% reusability of the adsorbents. The results of this study revealed that electrostatic attraction and ion exchange were the major mechanisms responsible for better

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efficiencies for adsorptive removal of arsenic. The evidence for the adsorption of arsenic contaminants was confirmed by FTIR analyses. The pseudo second order and Langmuir models were best suited to explain the adsorption of arsenic species on the surface of the as-synthesized metal-organic frameworks (MOFs). Based on the results, it was possible to conclude that the metal atoms in the synthesized MOFs had a minor impact on adsorption, since these MOFs presented identical results in the removal of arsenic species. This observation can be explained by the presence of a similar organic linker (2-methyl imidazole), which points to almost the same geometry and sponginess. However, there was a slight difference in the adsorption (organo-arsenic) removal achieved by the MOFs with different metal atoms.

Keywords: Arsenic removal, zeolitic imidazolate frameworks, metal organic frameworks, ZIF-MOFs, adsorption mechanism, adsorption removal, water purification

INTRODUCTION

Arsenic (As) is a metalloid element in nature that is highly toxic in its inorganic form. It is reported as one of the most significant chemical contaminants in groundwater. Unfortunately, arsenic impurities in ground and surface water have accumulated over time in the aqueous environment.^{1,2} According to statistics, 226 million people from 105 countries worldwide are suffering due to arsenic pollution and toxicity. In Bangladesh, Taiwan, Myanmar, Lao, West Bengal (India), Japan, Mongolia (China), Cambodia and Pakistan, studies showed elevated concentrations of arsenic in water.^{3,4} The existence of water pollution due to arsenic has been detected also in Chile, New Zealand, Hungary, Canada, USA, Poland, Mexico and Argentina,^{5,6} but the highest and most severe level of arsenic was found in Bangladesh, West Bengal (India), and in some parts of eastern Pakistan as well. In Halifax County, Nova Scotia (CA) and British Columbia (CA) incidents related to arsenic pollution in water have occurred, and arsenic pollution exceeding 3 mg L⁻¹ has been reported in the literature.^{3,7–9}

Long-term exposure to arsenic polluted water causes various diseases like cancer (skin, bladder, eye, uterus and respiratory system), arsenicosis, arthritis, jaundice, liver problems, chronic and acute toxicity and even death as reported in many studies.^{1,10} Arsenic species have high mobility and are easily accumulated in the aqueous environment as well as in the human body through the food chain, making arsenic a contaminant of concern worldwide. Uncontrolled anthropogenic activities, in addition to natural geochemical cycles, are the main conditions causing arsenic pollution. In the ground and wastewater, arsenic pollution occurs through natural processes such as the dissolution of rocks, ores, minerals and weathering or as a result of human activities such as gold and coal mining.^{11–13} Other human activities that produce a huge amount of arsenic in the ecosystem are industrial, oil refining, metal extractions, agricultural waste and irrigation, metal smelting, poultry feed/medicines and mineral/ores mining with typical concentrations in water ranging from 0.5 ppm to 100 ppm.^{14–16} WHO and USEPA have revised the permissible amount of arsenic in drinkable water, which is only 10 ppb (parts per billion). Arsenic naturally occurs in four different valences which are +5, +3, 0, and -3. However, in the ground and wastewater arsenic occurs mainly in two forms which are arsenite (+3) and arsenate (+5). According to the literature, the trivalent arsenic (arsenite) is the dominant form in groundwater due to the deficiency of oxygen while the pentavalent (arsenate) is the prevalent form in surface water due to excess of oxygen.^{13,17,18} Because of the high toxicity and mobility of arsenite in the environment, it is considered more toxic than arsenate. When the trivalent arsenic enters through an intermediate, it accumulates in the body of fish and humans and has more chances of producing arsenicosis.

There are many organoarsenic compounds available in the market used as herbicides, insecticides and pesticides. Adamsite (i.e., diphenylaminechloroarsine), also a medicine containing arsenic (structure and some properties are shown in Figure 1), is used as herbicides, insecticides, pesticides and in candles. It is also used as emetic agents and in poultry diseases.^{19–22}

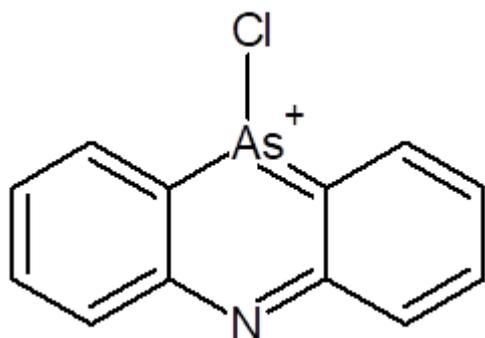


Figure 1. Structural formula of adamsite (diphenylaminechloroarsine) – organoarsenic having molar mass 277.58 g mol⁻¹, melting point 195 °C, chemical formula C₁₂H₉AsClN, CAS number 578-94-9, and IUPAC name 10-chloro-5,10-dihydrophenarsazine.

According to USEPA, many technologies are approved for the removal of arsenic species from water, such as i) precipitation, ii) adsorption, iii) ion exchange and iv) membrane separation. In addition to these, many other techniques are also applied, such as the use of zeolites, flocculation, chromatography, etc.²³ Among all these techniques, adsorption is recognized as one of the most popular and promising methods for removing pollutants, especially arsenic, due to its low cost, high specificity, ease of operation, non-toxicity and high efficiency, as also reported by Mohan and Pittman in their comprehensive review.²⁴

The removal and uptake efficiency of the adsorbents are directly related to their porosity and surface-to-volume ratio.²⁵ According to these criteria, metal-organic frameworks (MOFs) are excellent porous materials for decontamination of arsenic and other pollutants, catalytic conversion, catalysis, gas separation, storage, etc., due to their unique mechanical and chemical features, flexible/versatile designs, excellent chemical and thermal stability, high surface area, tunable porosity, and highly active sites that are easily accessible. Omar M. Yaghi and colleagues accomplished many pioneer works for the designing and synthesis of MOFs.²⁶

MOFs have proven to be excellent tools for the adsorption and separation of pollutants compared to traditional porous materials. Carbon-based materials and other porous materials are suitable for the decontamination caused by pollutants, but the cost of production and regeneration of these materials are very high, as reported by Mohan and Pittman.²⁴ On the other hand, MOF adsorbents, especially zinc and cobalt-based MOFs, are very cost-effective. In addition, zinc and cobalt-based MOFs have outstanding water stability, high pore size, ready availability, non-toxic metal source, and strong affinity to arsenic ions due to electrostatic interaction and π - π interaction, which make them very suitable as arsenic scavengers.²⁷⁻²⁹ Highly durable and robust, zinc and cobalt-based MOFs will extend their use in the water purification field.³⁰

In this paper, we report our as-synthesized zeolitic imidazolate frameworks, named ZIF-8 and ZIF-67, in which 2-methylimidazole binds to zinc and cobalt metal ions, respectively, which act as coordinately central metal atoms. ZIF-8 and ZIF-67 are structurally featured by high thermal and chemical stability, tunable porosity, high surface area and sufficient active sites, features that make them very suitable for their applications. Due to continuously increasing levels of arsenic in ground drinking water, there should be an urgent need to explore practical and effective technologies to remove arsenic species from aquatic environment. Moreover, ZIF-8 and ZIF-67 are hydrophobic materials widely used for the adsorption process. So, we synthesized these materials and compared them in terms of their adsorption capacity and removal efficiency to remove an organo-arsenic specie (adamsite) from water. In this study we also demonstrate adsorption mechanism for the adsorption of arsenic species from water as well as isothermal and kinetic studies. The adsorption mechanism includes electrostatic enhancement, and hydrophobic and π - π interactions.

MATERIALS AND METHODS

All the chemicals used were AR Grade. Zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O], cobalt(II) nitrate hexahydrate [Co(NO₃)₂·6H₂O], sodium arsenate [Na₃AsO₄·12H₂O] for As(V), sodium arsenite [NaAsO₂]

for As(III), 2-methyl imidazole, methanol, HCl and NaOH were obtained from Merck, BDH, and used as received, without further purification. Adamsite was obtained from the local market of Bahawalpur, Punjab, Pakistan. For the washing and synthesis procedures, ultra-pure water was used.

Standard solutions with 1000 mg L⁻¹ of adamsite, sodium arsenite and sodium arsenate were prepared and subsequently used for the preparation of solutions with 10, 15, and 20 mg L⁻¹, respectively.

Synthesis of Cobalt/Zinc MOFs

ZIF-8 and ZIF-67 materials were prepared according to reported literature,^{30,31} with certain modifications. According to a typical method for the synthesis of ZIF-67 and ZIF-8, 1 mmol of metal salts (Zn/Co nitrate hexahydrate) was added in a minimal quantity of ultra-pure water in beakers. 4 mmol of 2-methyl imidazole was mixed in a minimal amount of methanolic solution and mixing was done using a stirrer. Then, these metal salt and imidazole solutions were mixed slowly under continuous stirring at ambient temperature (25 ± 2 °C) for 30 minutes. After stirring, the mixture was left for 60 minutes to complete the processing of crystal aging. After aging, the crystals were washed 3 times with a mixture of water and methanol (1:1) and centrifuged at 6000 rpm for 10 minutes to remove unreacted reagents. These washed crystals were dried overnight in an oven at 100 °C.

Characterization of Cobalt/Zinc MOFs

The synthesized ZIF-8 & ZIF-67 nanoparticles were characterized by the following advanced spectroscopic techniques: powder X-ray diffractometry (P-XRD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller technique (BET) and Fourier transform infrared spectroscopy (FTIR). To obtain FTIR spectra, the attenuated total reflectance (ATR) technique and a Bruker FTIR instrument with a range of 400-4000 cm⁻¹ were used. The surface morphology of the synthesized MOFs was studied using a JSM-7800F scanning electron microscope from JEOL. The crystalline nature of ZIF-8 was observed by the P-XRD technique. The surface area and porosity of the material were checked using the BET technique at 77.3 K using the Quadrasorb2MP, Quantachrome surface analyzer. The Perkin Elmer AAnalyst 100 AAS was used to determine arsenic species before and after the adsorption procedure.

Adsorption experiments

Adsorption experiments were performed by mixing a certain amount of adsorbent with a specific volume of the arsenic solution; the resulting mixture was stirred in constant rotation and at room temperature (25 ± 2 °C). At the end of the experiments, the adsorbent was separated by filtration with syringe filter paper and the arsenic concentration in the filtrate was determined by atomic absorption spectroscopy (AAS).

The effect of pH on adsorption was studied by adding 10 mg of the adsorbent to 10 mL of arsenic solution (10 mg L⁻¹). The pH was adjusted using 0.1 M solutions of NaOH and HCl and the contact time was 2 h. The adsorbents showed maximum arsenic species removal efficiency (90.5%) at pH 7.8, so this optimized pH was used for further experiments.

In the following experiments, the concentration of the arsenic species was changed from 10 to 15 and 20 mg L⁻¹, and the solution volume was fixed at 250 mL with a contact time of 6 h.

Adsorption capacity q_e (mg g⁻¹) and removal efficacy were calculated by applying equations 1 and 2, respectively.

$$q_e = (C_o - C_e)V/W \quad (1)$$

$$\text{Removal efficiency (\%)} = (C_i - C_e) / C_i * 100 \quad (2)$$

where, C_i and C_o are the concentration of arsenic species (mg L⁻¹) before the adsorption process; C_e is the concentration of arsenic species after the adsorption process; W is the mass (g) of adsorbent (ZIF-8, ZIF-67) and V is the volume (L) of the solution.

The Langmuir and Freundlich models were also applied in the adsorption kinetics study to confirm the adsorption process. The pseudo second order and pseudo first order kinetics were also applied and they are expressed as linear functions using equations 3 and 4 respectively.

$$\ln Q_e - Q_t = \ln Q_e - K_1 t \quad (3)$$

$$t/Q_t = t/Q_e + 1/K_2 Q_e^2 \quad (4)$$

Q_e = quantity of arsenic adsorbed at equilibrium

Q_t = quantity of arsenic adsorbed in a time interval

t (h) = adsorption time in hours

K_1 (h^{-1}) = rate constant of pseudo 1st order

K_2 ($g\ mg^{-1}\ h^{-1}$) = rate constant of pseudo 2nd order

Values of K_1 and Q_e were determined from plotting $\ln(Q_e - Q_t)$ vs time (t). K_1 = slope and $\ln Q_e$ = intercept

K_2 value was determined by plotting the t/Q_t vs time

The initial adsorption rate ($h = mg\ g^{-1}\ min^{-1}$) can be calculated from equation 5 and the half adsorption time ($t_{0.5}$, h) from equation 6.

$$h = K_2 Q_e^2 \quad (5)$$

$$t_{0.5} = 1/K_2 Q_e \quad (6)$$

Evaluation of the reusability of the synthesized MOFs

To evaluate the regeneration of the adsorbent after a removal experiment of a solution containing 10 $mg\ L^{-1}$ of arsenic, the adsorbent separated by filtration was washed with deionized water and added to 100 mL of an eluent solution containing NaOH (2 M), HCl (0.1 M) and NaCl (2 M) in a 2:7:1 ratio. This mixture of adsorbent and eluent was stirred for 120 minutes at 250 rpm at room temperature ($25 \pm 2\ ^\circ C$) and the adsorption capacity as well as removal efficiency of the adsorbent was calculated using equations (1) & (2). This procedure was repeated 5 times.³²

RESULTS AND DISCUSSION

FTIR spectra of the ZIF-8 and ZIF-67 MOFs are presented in Figures S1-S4 in which bands at 2817 cm^{-1} and 1566 cm^{-1} are observed. These bands correspond to stretching vibrations of -CH and -CN groups present in imidazole rings in ZIF-8 and ZIF-67 MOFs. Many other typical bands at about 3329 cm^{-1} , 684 cm^{-1} , 617 cm^{-1} and 432 cm^{-1} are also present, indicating the presence of -OH, Zn-O, Zn-N, and Co-N bonds, respectively in the MOFs. After the adsorption of arsenic species, FTIR spectra were also performed, and the results confirm that adsorption of arsenic species takes place successfully as indicated by the stretching vibrations at 832 cm^{-1} , 924 cm^{-1} , 3633 cm^{-1} and 3737 cm^{-1} . These vibrations are exhibited due to the interactions among the arsenic species and the ZIF-8 and ZIF-67 MOFs. From the FTIR study, it was concluded that the adsorption of arsenic species on the surface of MOFs takes place successfully, as vibrations in the FTIR spectrum at 832 cm^{-1} and 924 cm^{-1} are typically shown by As-O bonds present in MOFs after the adsorption process.³²

From the powder XRD analysis, it was confirmed that the MOFs showed crystallinity, lattice structure and uniform morphology (Figure 2). The main peaks in Figure 2-b and 2-d closely matched with reported study.^{30,33,34} From the scanning electron microscopy (SEM) results, it was shown that the ZIF-8 MOF have cubic and ZIF-67 have polyhedral geometry, which also gives a strong indication for the synthesis and purity of ZIF-8 & ZIF-67 nanoparticles (Figure 2).

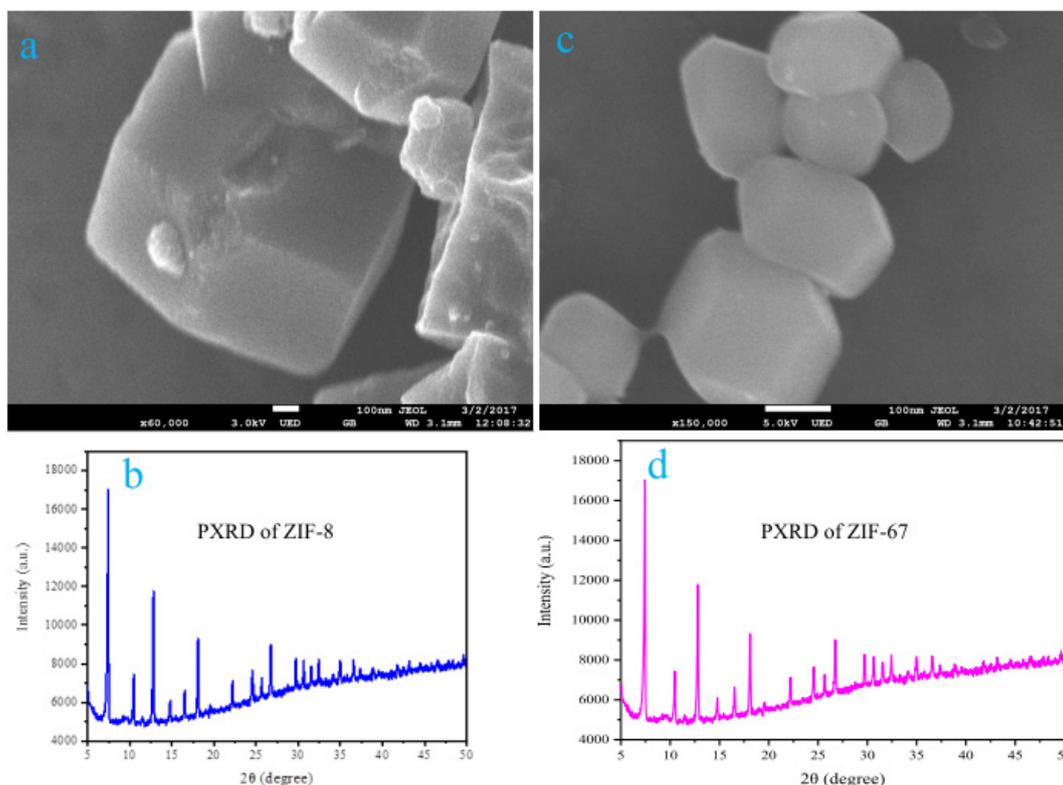


Figure 2. Morphology of ZIF-8 MOF which is cubic (a) and ZIF-67 MOF which is polyhedral (c) shown by SEM; Powder XRD pattern of ZIF-8 (b) and ZIF-67 (d). [Reprinted from *Food Chem. Toxicol.* **2021**, 149, 112008. Ahmad, K.; Shah, H.-R.; Ashfaq, M.; Shah, S. S. A.; Hussain, E.; Naseem, H. A.; Parveen, S.; Ayub, A. Effect of metal atom in zeolitic imidazolate frameworks (ZIF-8 & 67) for removal of Pb^{2+} & Hg^{2+} from Water. <https://doi.org/10.1016/j.fct.2021.112008> Copyright© (2022), with permission from Elsevier.]

From the Brunauer-Emmett-Teller (BET) analysis, the pore size ratio and porosity were calculated. The nitrogen adsorption/desorption curves in Figure 3 indicate that these MOFs have high surface area and are nanoparticles, which means that ZIF-8 & ZIF-67 are highly porous materials. The porosity is directly related to the separation and adsorption capacity of the material for the removal of contaminants.

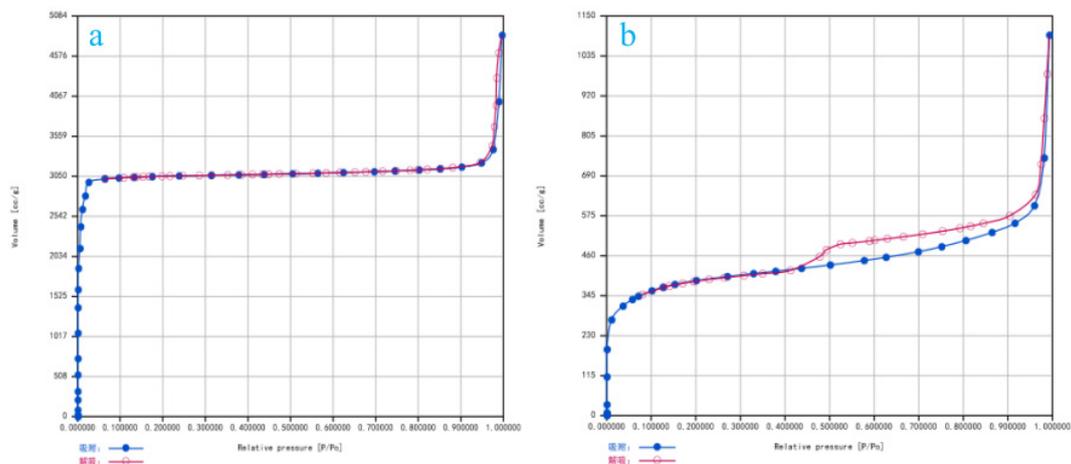


Figure 3. Nitrogen adsorption/desorption curves of ZIF-8 (a) and ZIF-67 (b).

Adsorption Studies

Effect of pH

The adsorption capacity of the synthesized MOFs was tested at different pH values. ZIF-8 & ZIF-67 showed maximum adsorption capacities for adsorbate, As(III) and As(V) at pH 7.8, what can be explained by the negatively and positively charged sphere in ZIF-67 & ZIF-8 at pH 7.8. The maximum adsorption capacity was 70.29 & 62.01, 71.49 & 70.92, 87.03 & 86.70 mg g⁻¹ for adsorbate, arsenite and arsenate, respectively, at pH 7.8. From this experiment, it was supposed that π - π and electrostatic interactions are the main forces that operate between MOFs and arsenic species (Figures 4–5 and Figures S5–S8).

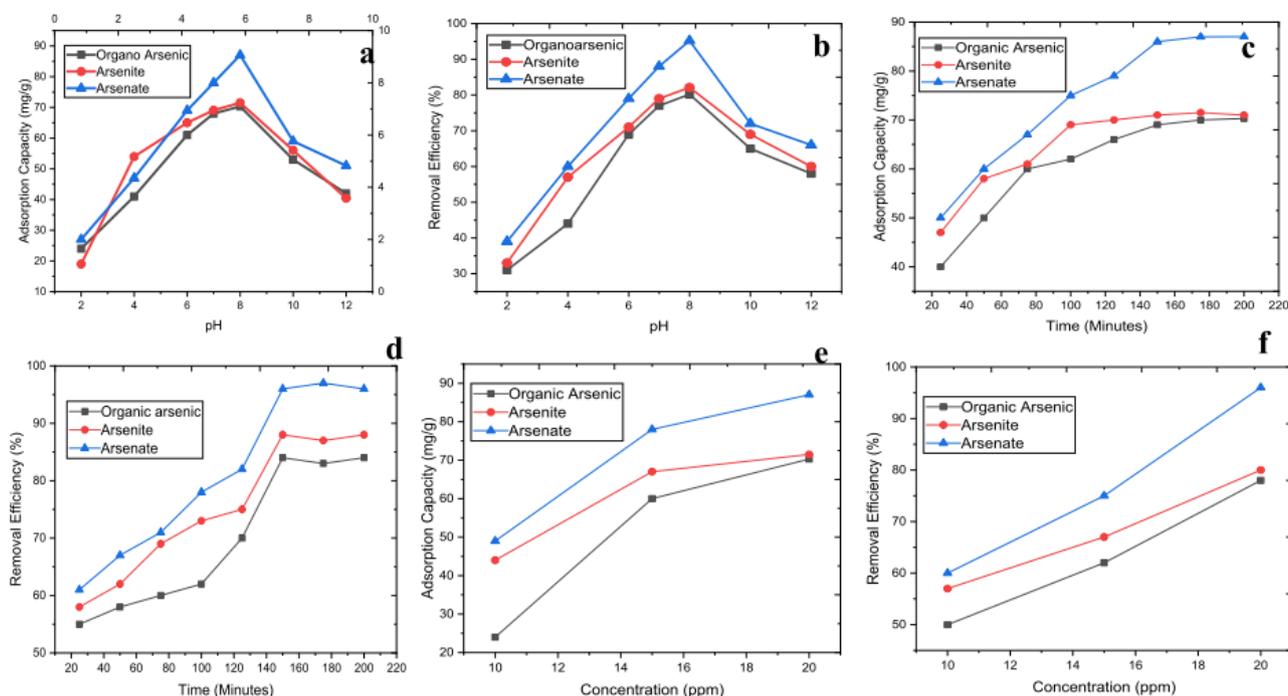


Figure 4. a) Adsorption capacity of ZIF-8 at acidic/basic and neutral pH; b) Removal efficiency of ZIF-8 at different pH values; c) Adsorption capacity of ZIF-8 vs time (minutes); d) Removal efficiency of ZIF-8 vs time (minutes); e) Adsorption capacity of ZIF-8 against different concentrations (10, 15 and 20 mg L⁻¹) of arsenic solutions in water; f) Removal efficiency of ZIF-8 against different concentrations (10, 15 and 20 mg L⁻¹) of arsenic solutions in water.

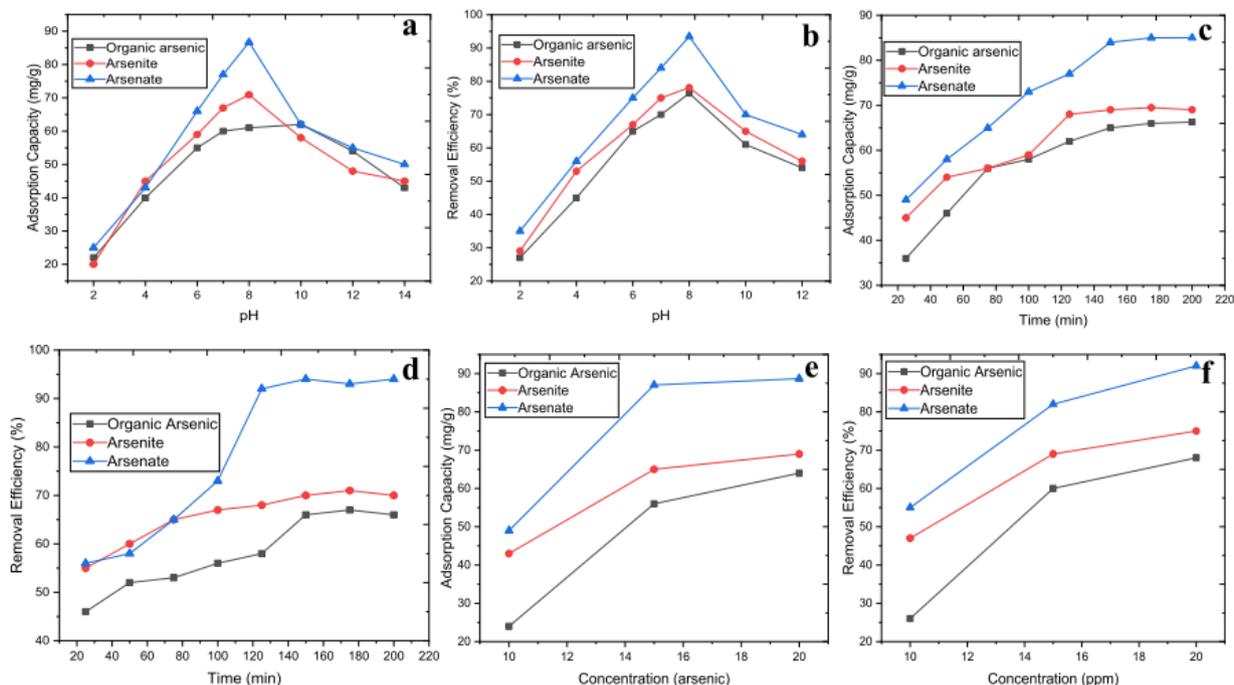


Figure 5. a) Adsorption capacity of ZIF-67 at acidic/basic and neutral pH. b) Removal efficiency of ZIF-67 at different pH. c) Adsorption capacity of ZIF-67 Vs time (minutes). d) Removal efficiency of ZIF-67 Vs time (minutes). e) Adsorption capacity of ZIF-67 against different concentrations (10, 15 and 20 mg L⁻¹) of arsenic solutions in water. f) Removal efficiency of ZIF-67 against different concentrations (10, 15 and 20 mg L⁻¹) of arsenic solutions in water.

To investigate the MOFs' stability and the ion exchange mechanism, 0.5 g of MOFs were added to 50 mL of ultra-pure water, sonicated for 30 minutes to form a suspension, and left for 6 hours. After that, filtration was done followed by centrifugation for 10 minutes. The amount of cobalt and zinc metal in the solutions were measured by atomic absorption spectrometry. The amount determined was 0.0003 g L⁻¹, which assumes that these MOFs are highly water stable and exchange their metal ions to a very low extent. To confirm the ion exchange mechanism, it was observed that at pH ≤ 5 these MOFs contain negative charge. As the arsenic species arsenite and arsenate exist in water in the anionic form and these MOFs at pH < 5 also contain negative sphere, these same charges should be repelled and there will be practically no adsorption at pH < 5. However, in the pH experiments, it was observed that at pH < 5 adsorption of arsenic also occurred. Consequently, from the results, it was concluded that in addition to the electrostatic interaction, the ion exchange interaction also occurs, which is responsible for this adsorption of arsenic species even with the same charges.^{20,35}

Effect of contact time

The adsorption capacity of ZIF-8 & ZIF-67 was also studied at different time intervals to check the effect of removal efficiency with time. In the beginning, the removal of arsenic was very sharp and after 1 hour this process was slowed down and then reached equilibrium after 3 hours. Initially, the adsorption process was very fast due to the availability of maximum surface area and arsenic metal, but in the course of time, the availability of pores and arsenic metal ions decreased, hence the adsorption capacity also decreased.^{36,37} The maximum adsorption capacity of ZIF-8 & ZIF-67 was 70.29 & 62.01, 71.49 & 70.92, 87.03 & 86.70 mg g⁻¹ at equilibrium time of 3 hours with 20 mg L⁻¹ solutions of adamsite, arsenite and arsenate, respectively. These results of removal efficiency and adsorption capacity *versus* time are shown in Figures 4–5 and Figures S9–S12.

Effect of initial concentration of arsenic species

The effect of the concentration of arsenic species on the adsorption capacity was also studied. For this purpose, solutions of varying concentrations were prepared, such as 10, 15, and 20 mg L⁻¹ of adamsite, arsenite and arsenate, and an adsorbent dose of 1 g L⁻¹ was used. From the concentration effect study, it was observed that as the concentration of arsenic species is increased from 10 – 20 mg L⁻¹ the adsorption capacity of arsenic is also increased but removal efficiency decreased. The increase in the adsorption capacity was due to the availability of more and more arsenic ions in the solution which increases the adsorption of arsenic on the surface of MOFs (Figures 4–5 and Figures S13–S16).³⁸ Furthermore, it was observed that the adsorption capacity is directly proportional to the concentration of arsenic species, while the removal efficiency is inversely related to the concentration of these arsenic ions.³⁹

Adsorption Kinetics

For explanation of the adsorption process with MOFs, pseudo 1st and 2nd order models were applied. It was observed that pseudo 2nd order is best fitted for adsorption of arsenic species, since the R² values for adamsite, arsenite and arsenate are high, namely: 0.9901 & 0.99087, 0.97013 & 0.9929, 0.9947 & 0.9975, respectively. As correlation coefficient value for pseudo 2nd order is maximum, it can be inferred that chemisorption or chemical adsorption of arsenic species takes place using MOFs. Chemical adsorption means that functional groups such as the amine group present in the MOFs are responsible for the adsorptive elimination of arsenic species from water. Besides chemical adsorption, the ion exchange process is also involved for the efficient removal of arsenic.²² The graphical representation of kinetic models is given in Figure 6, Figures S17–S20 and Tables I–II.

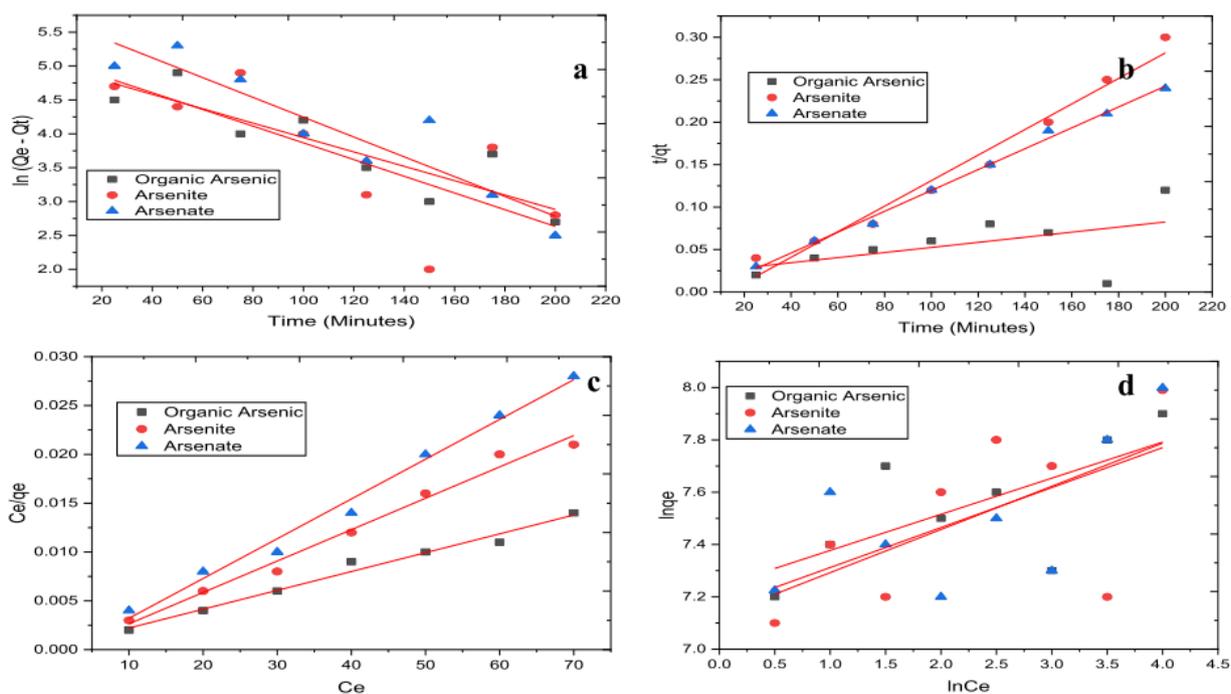


Figure 6. a) Kinetic parameters for the pseudo first order kinetics model for the removal of arsenic using ZIF-8, b) Kinetic parameters for the pseudo second order kinetics model for the removal of arsenic using ZIF-8, c) Adsorption isotherm fitted by Langmuir Model, d) Adsorption isotherm fitted by Freundlich Model.

Table I. Kinetic parameters (pseudo first order and second order equations) for adsorption process using ZIF-8

Arsenic Species	Pseudo First Order				Pseudo Second Order				
	Q_e (mg g ⁻¹)	K_1 (h ⁻¹)	R ²	Pearson value	Q_e (mg g ⁻¹)	K_2 (g mg ⁻¹ h ⁻¹)	R ²	Q_e exp (mg g ⁻¹)	Pearson value
Organic Arsenic	58.66	2.3126	0.73081	0.70511	62.01	0.0577	0.99011	70.49	0.92451
As(III)	63.39	2.8932	0.49049	0.51472	68.78	0.0611	0.97013	71.29	0.98711
As(V)	71.10	3.0765	0.83125	0.85149	74.84	0.0687	0.99477	87.03	0.99775

Table II. Kinetic parameters (pseudo first order and second order equations) for adsorption process using ZIF-67

Arsenic Species	Pseudo First Order				Pseudo Second Order				
	Q_e (mg g ⁻¹)	K_1 (h ⁻¹)	R ²	Pearson value	Q_e (mg g ⁻¹)	K_2 (g mg ⁻¹ h ⁻¹)	R ²	Q_e exp (mg g ⁻¹)	Pearson value
Organic Arsenic	57.21	4.90714	0.73081	0.68521	62.01	0.0577	0.99011	76.21	0.99594
As(III)	62.01	5.009	0.56328	0.71421	70.92	0.0611	0.97013	78.12	0.99686
As(V)	86.70	5.60714	0.85535	0.80123	79.57	0.0687	0.99477	88.71	0.9989

Adsorption isotherm

To explain the isothermal adsorption, the Freundlich and Langmuir models were applied. The Langmuir model was best fitted having R² values for adamsite, arsenite and arsenate being 0.97898 & 0.98577, 0.98306 & 0.99356, 0.98577 & 0.99771, respectively. The linear plots of these models are presented in Figure 6, Figures S21–S24 and Tables III–IV. This experiment revealed that MOFs prescribe monolayer adsorptive removal of adamsite, arsenite and arsenate due to the higher surface area, large functionality,⁴⁰ open metal and pore sites, and exhibited maximum adsorption capacity in a very short time as compared to other MOFs, as given in Table V.

Table III. Langmuir and Freundlich model parameters using ZIF-8

Arsenic Species	Langmuir Model				Freundlich Model		
	Q_e (mg g ⁻¹)	K_L (L mg ⁻¹)	R ²	Pearson Value	K_F (mg g ⁻¹)	R ²	Pearson value
Organic Species	70.49	0.4258	0.97898	0.9912	59.23	0.38955	0.69048
As(III)	71.29	0.0292	0.98306	0.9929	61.12	0.29014	0.62574
As(V)	87.03	0.0337	0.98577	0.9941	74.70	0.34001	0.29014

Table IV. Langmuir and Freundlich model parameters using ZIF-67

Langmuir Model					Freundlich Model		
Arsenic Species	Q_e (mg g ⁻¹)	K_L (L mg ⁻¹)	R ²	Pearson Value	K_F (mg g ⁻¹)	R ²	Pearson value
Organic Species	62.01	0.4101	0.98577	0.99405	57.11	0.11979	0.20045
As(III)	70.49	0.0287	0.99356	0.99731	60.58	0.15415	0.10356
As(V)	86.70	0.0371	0.99771	0.99904	78.19	0.14091	0.51345

Table V. Comparison of adsorption of As (III), As (V) and organic arsenic using ZIF-8 & ZIF-67 with other adsorbents reported in the literature

Adsorbent	pH	Concentration (mg L ⁻¹)	Adsorption Capacity (mg g ⁻¹)			Ref.
			As (III)	As (V)	Organic As	
Fe-Chitosan Flakes	7.0	1 – 10	16.15	22.47	-	41
Fe-Coated Zeolites	4.0	0 – 20	-	0.68	-	42
Activated Alumina	7.0	0 – 250	19.63	-	-	43
Fe-Zr Binary Oxide	7.0	0.5 – 15	-	9.36	-	44
Fe-Mn Binary Oxide	6.9	0 – 40	100.4	53.90	-	45
CuO Nanoparticles	8.0	0.1 – 100	26.9	22.60	-	46
Treated Laterite	7.0	0.2 – 20	9.4	21.60	-	47
ZrO ₂ ·xH ₂ O	7.0	0.3 – 100	47.1	29.30	-	48
Fe ₃ O ₄	7.0	0 – 100	5.68	4.78	-	49
ZIF-8	6.0-8.0	0 – 20	71.49	87.03	70.29	This Study
ZIF-67	6.0-8.0	0 – 20	70.92	86.70	62.01	This Study

Adsorption mechanism

Adsorption is a surface-based exothermic process in which molecules of a compound in the gaseous or liquid state are accumulated on an adsorbent surface. During adsorption, two main processes are involved, such as physical adsorption (physisorption or adsorptive adsorption) and chemical adsorption (chemisorption or reactive adsorption). Adsorption is caused by London dispersion forces, a type of van der Waals force that exists between molecules and acts in the same way as gravitational forces between planets. The adsorption process is always exothermic because surface particles of the adsorbent are unstable and when the adsorbate is adsorbed on the surface, the energy of the adsorbent decreases and this results in heat evolution.⁴¹⁻⁴⁶ For the explanation of the adsorption process for arsenic removal, FTIR analyses were also performed after the adsorption process. The spectra obtained show peaks in the range

of 832 cm^{-1} , 924 cm^{-1} , 3637 cm^{-1} and 3737 cm^{-1} which are exhibited due to interactions among arsenic species and MOFs (Figures S1–S4). Therefore, the FTIR results indicate that MOFs are successfully formed and adsorb arsenic species on their surfaces due to the presence of the NH group.^{47–50} Furthermore, the bands in the FTIR spectrum at 832 cm^{-1} and 924 cm^{-1} are typically presented by MOFs due to As-O bonds after the adsorption of arsenic.³² Figure 7 presents the proposed adsorption mechanism.

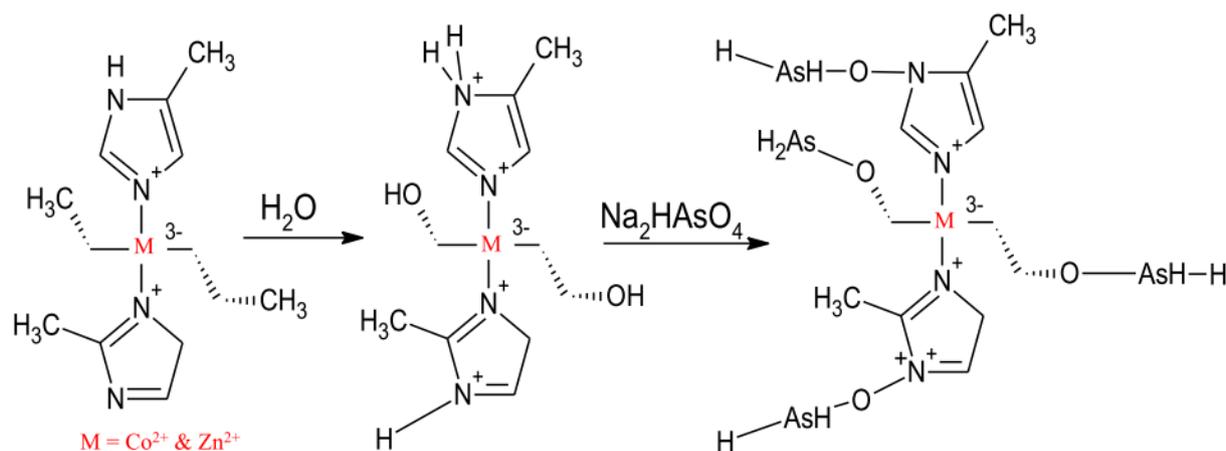


Figure 7. Proposed adsorption mechanism for the removal of arsenic species using ZIF-8 & ZIF-67.

Reusability of the synthesized MOFs

From the regeneration experiments, it was observed that the ZIF-67 and ZIF-8 MOFs exhibited regeneration up to 95% and 92% respectively (Figure S25), which indicates that these MOFs can be repeatedly applied for the removal of arsenic species present in water.^{45,51,52}

CONCLUSION

In summary, the synthesis of ZIF-8 and ZIF-67 via hydrothermal technique was achieved and the MOFs obtained were considered suitable for the removal of arsenic metal ions from aqueous solution. The adsorption capacities of the synthesized MOFs were 70.29 & 62.01, 71.49 & 70.92, 87.03 & 86.70 mg g^{-1} for adamsite, arsenite and arsenate, respectively, which represent excellent adsorption capacities as compared to other adsorbents. This adsorption capacity is mainly due to three reasons: porosity of adsorbents which capture the arsenic species tightly to bind with ZIF-8 and ZIF-67, the MOFs' high surface area, and van der Waals forces. The ZIF-8 & ZIF-67 MOFs exhibited similar arsenic adsorption capacities due to the presence of the same organic ligand (2-methyl imidazole) and the same geometry, shape, pore size and porosity. There is a slight decrease in the adsorption capacity in the case of adamsite removal that can be explained due the presence of different central metal atoms, i.e. zinc in ZIF-8 and cobalt in ZIF-67. The regeneration procedures revealed that these MOFs can be applied repeatedly for arsenic removal from water. These results indicate that ZIF-8 and ZIF-67 are the most efficient MOFs for eliminating inorganic and organic arsenic from water solutions. From this work, it is suggested that future studies should be carried out for the applications of these MOFs for the removal of arsenic species in wastewater.

According to our information, this is the first study in which the assessment between ZIF-8 and ZIF-67 is explored for the removal of organic and inorganic arsenic species from water.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgment

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SUPPLEMENTARY MATERIAL

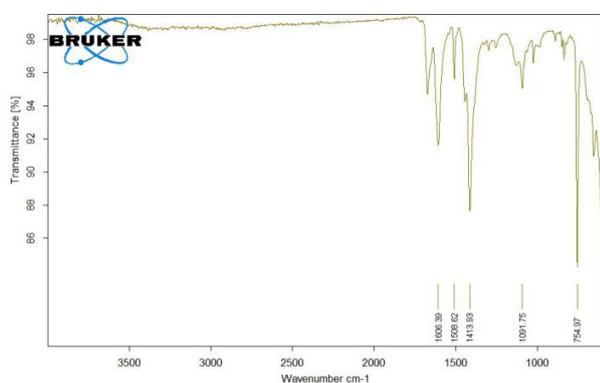


Figure S1. FTIR spectrum of ZIF-67 before the adsorption of Arsenic.

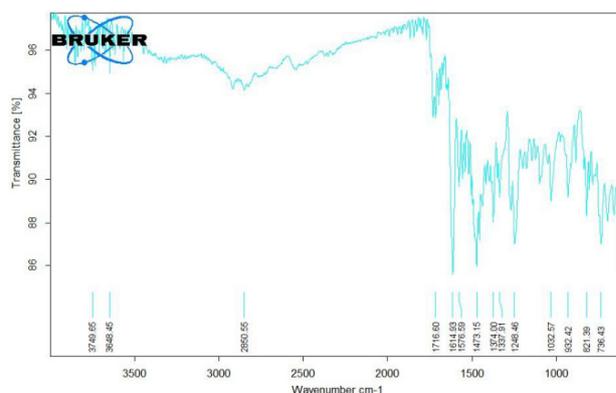


Figure S2. FTIR spectrum of ZIF-67 after the adsorption of Arsenic.

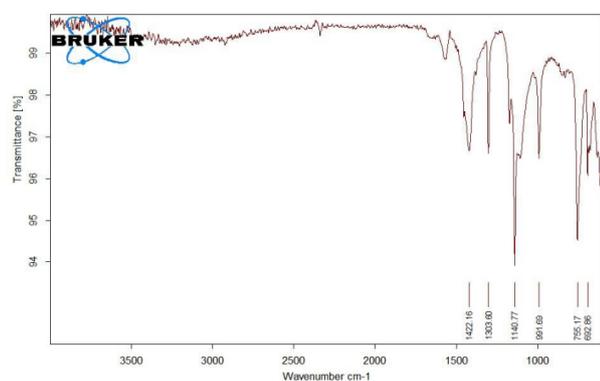


Figure S3. FTIR spectrum of ZIF-8 before the adsorption of arsenic.

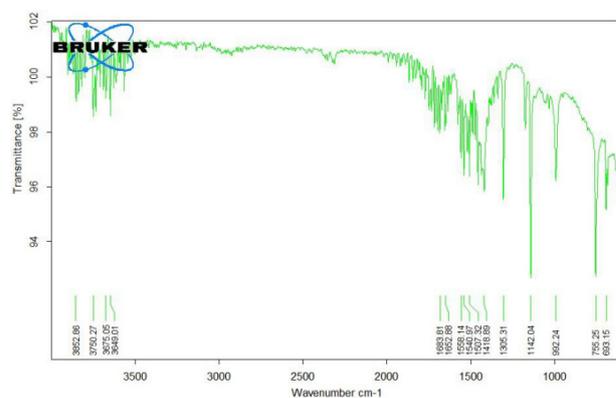


Figure S4. FTIR spectrum of ZIF-8 after the adsorption of arsenic.

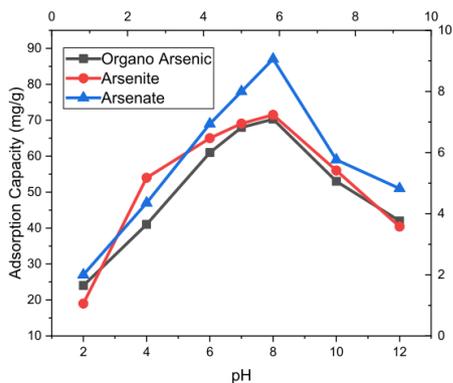


Figure S5. Adsorption capacity of organo arsenic, arsenite and arsenate using ZIF-8 at different pH.

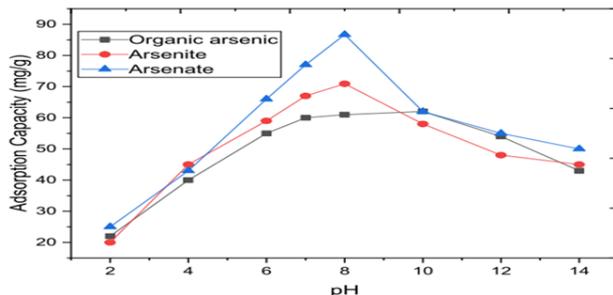


Figure S6. Adsorption capacity of organo arsenic, arsenite and arsenate using ZIF-67 at different pH.

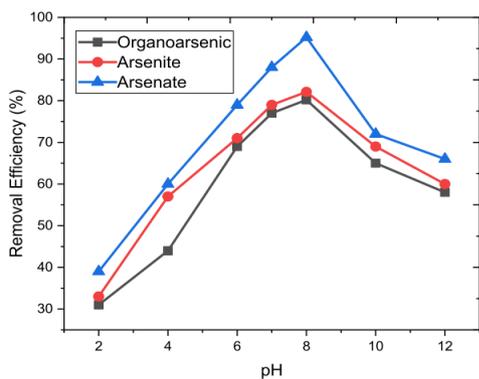


Figure S7. Removal efficiency of organo arsenic, arsenite and arsenate using ZIF-8 at different pH.

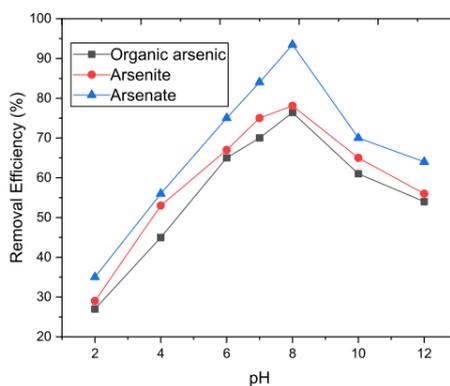


Figure S8. Removal efficiency of organo arsenic, arsenite and arsenate using ZIF-67 at different pH.

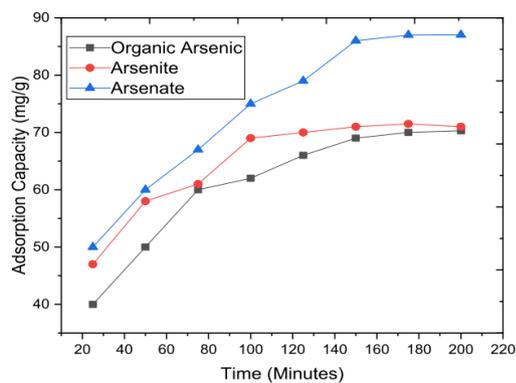


Figure S9. Adsorption capacity vs time for arsenic species using ZIF-8.

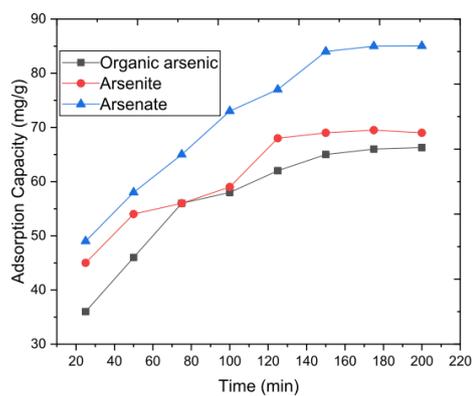


Figure S10. Adsorption capacity vs time for arsenic species using ZIF-67.

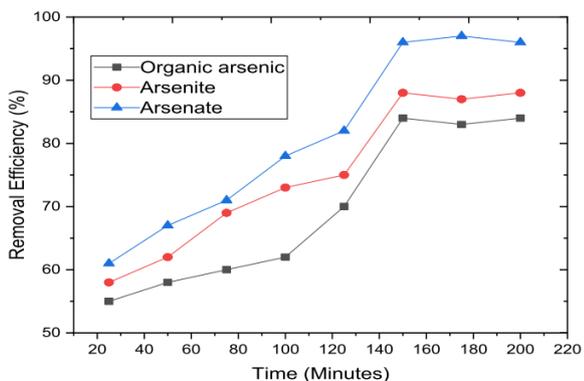


Figure S11. Removal efficiency vs time for arsenic species using ZIF-8.

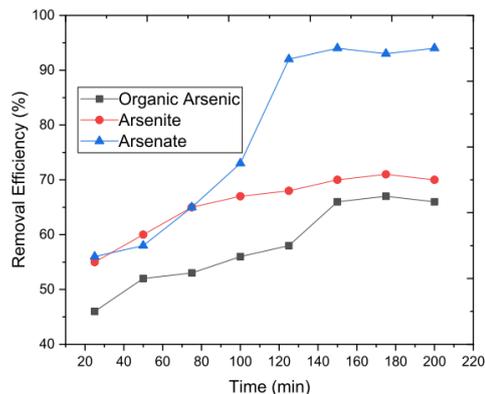


Figure S12. Removal efficiency vs time for arsenic species using ZIF-67.

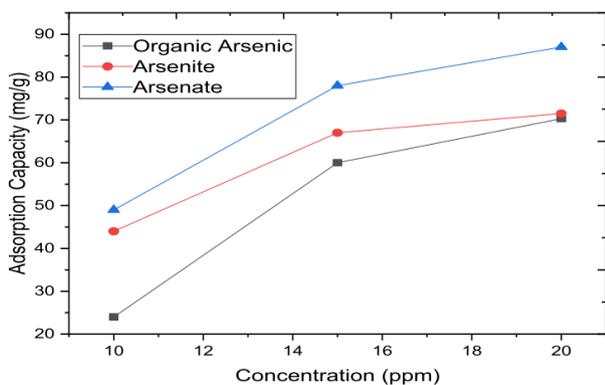


Figure S13. Adsorption capacity vs concentration for arsenic species using ZIF-8.

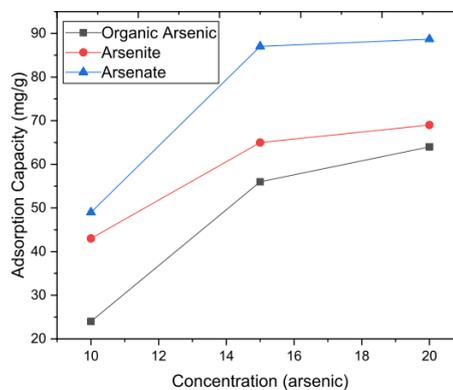


Figure S14. Adsorption capacity vs concentration for arsenic species using ZIF-67.

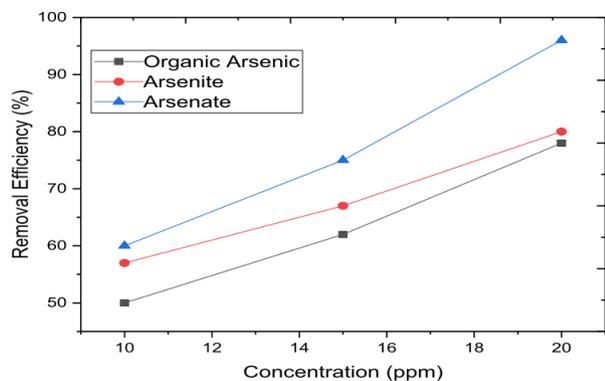


Figure S15. Removal Efficiency vs concentration for arsenic species using ZIF-8.

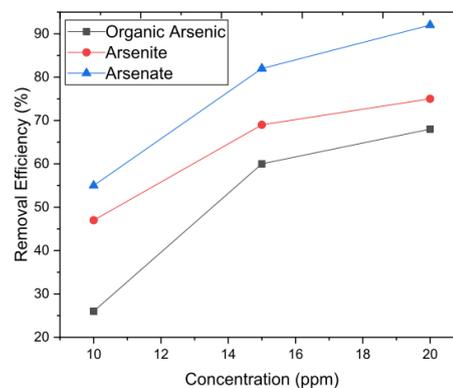


Figure S16. Removal Efficiency vs concentration for arsenic species using ZIF-67.

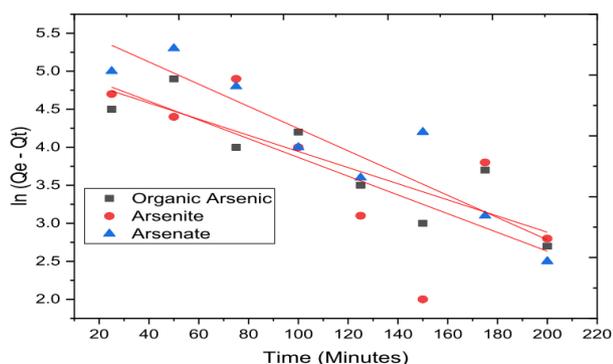


Figure S17. Kinetic parameters for the pseudo first order kinetics model for the removal of arsenic using ZIF-8.

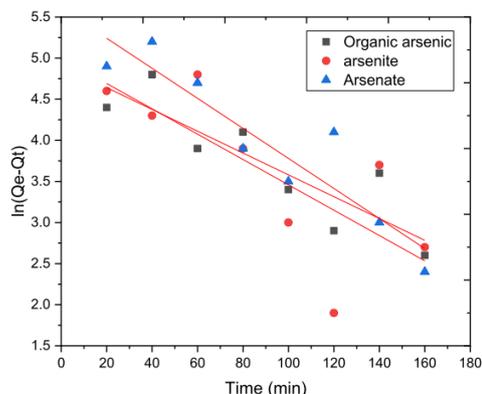


Figure S18. Kinetic parameters for the pseudo first order kinetics model for the removal of arsenic using ZIF-67.

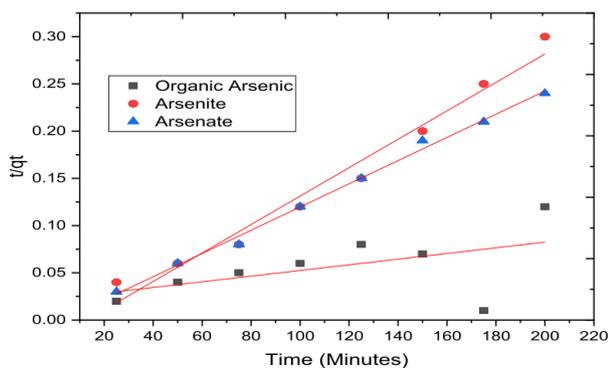


Figure S19. Kinetic parameters for the pseudo second order kinetics model for the removal of arsenic using ZIF-8.

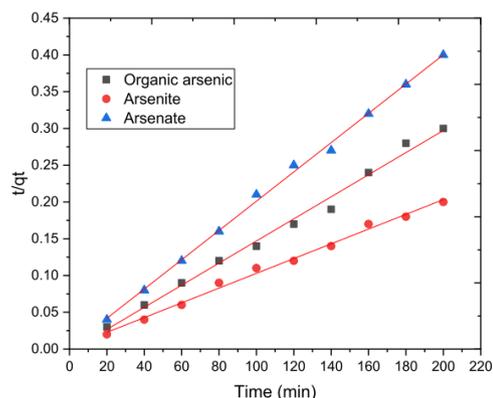


Figure S20. Kinetic parameters for the pseudo second order kinetics model for the removal of arsenic using ZIF-67.

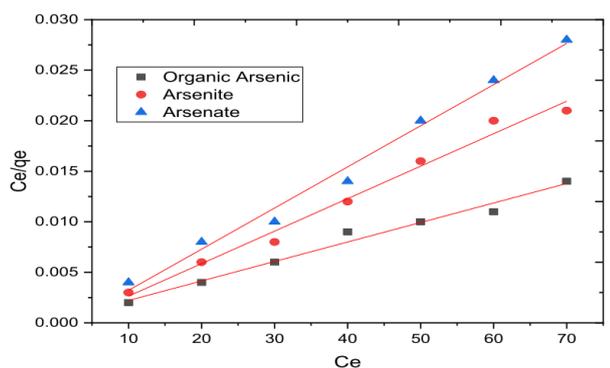


Figure S21. Adsorption isotherm fitted by Langmuir Model using ZIF-8.

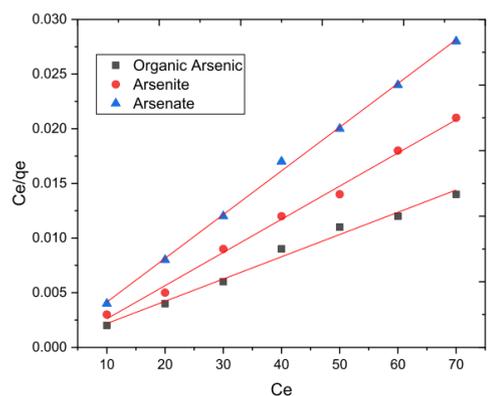


Figure S22. Adsorption isotherm fitted by Langmuir Model using ZIF-67.

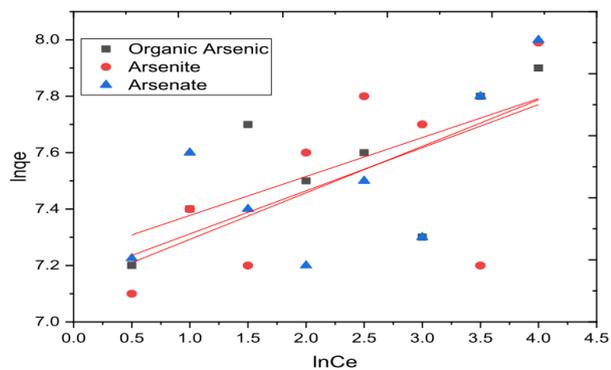


Figure S23. Adsorption isotherm fitted by Freundlich Model using ZIF-8.

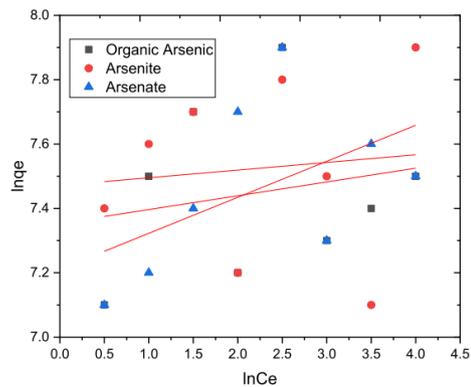


Figure S24. Adsorption isotherm fitted by Freundlich Model using ZIF-67.

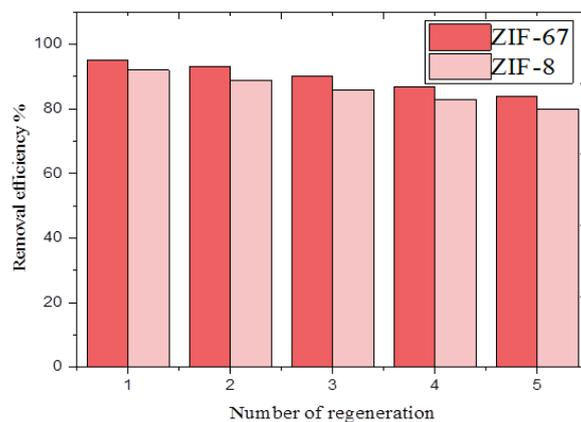


Figure S25. Regeneration of ZIF-67 & ZIF-8 up to five times and shows 95% removal efficiency.