



## Arsenic adsorption from aqueous solution on synthetic zeolites

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### ABSTRACT

The adsorption of arsenic from aqueous solution on synthetic zeolites H-MFI-24 (H24) and H-MFI-90 (H90) with MFI topology has been investigated at room temperature (r.t) applying batch equilibrium techniques. The influences of different sorption parameters such as contact time, solution pH, initial arsenic concentration and temperature were also studied thoroughly in order to optimize the reaction conditions. The adsorption of arsenic on to H24 and H90 follows the first-order kinetics and equilibrium time was about 100 min for both the adsorbents. The first-order rate constant ( $k$ ),  $4.7 \times 10^{-3} \text{ min}^{-1}$  for H90 is more than two times higher in magnitude compared to  $2.1 \times 10^{-3} \text{ min}^{-1}$  for H24. Adsorption performance of H90 is higher compared to H24 due to its highly mesoporous nature which in turn accelerates the diffusion process during adsorption. As(V) sorption capacity derived from Langmuir isotherm for H24 and H90 are 0.0358 and 0.0348  $\text{g g}^{-1}$ , respectively. Arsenic uptake was also quantitatively evaluated using the Freundlich and Dubinin–Kaganer–Radushkevich (DKR) isotherm models. Ion exchange between adsorbent's terminal aluminol groups with different predominant forms of arsenate in solution is one of the various important reactions occurred during adsorption process.

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### 1. Introduction

The contamination of natural and wastewater by different pollutants in the environment is a major concern worldwide and consequently much attention has been aroused in abatement of such pollutants [1–3]. Arsenic is one of the contaminants found in the environment which is notoriously toxic to man and other living organisms [4–6]. It is a matter of worry that although WHO lowered the guideline value for arsenic from 50 to 10 ppb, some countries like Bangladesh and China still have 50 ppb arsenic in drinking water [7]. The presence of arsenic in ground water is mostly due to minerals dissolving naturally from rocks and soils [8,9]. Moreover, biological and mining activities, geochemical reactions, volcanic emissions, use of arsenic additives, pesticides, herbicides and crop desiccants make the problem more serious for animal and human beings [9,10]. Arsenic-contaminated water may cause numerous diseases of the skin and internal organs [8,9,11–13]. An inorganic form of arsenic is highly toxic compared to organic arsenic [4,14]. Inorganic arsenate ( $\text{AsO}_4^{3-}$ ) and arsenite ( $\text{AsO}_3^{3-}$ ), referred to a As(V) and As(III) are most common in natural waters. Although, As(V) tends to be less toxic compared to that of As(III), it is thermodynamically more stable due to which it predominates under normal conditions and becomes the cause

of major contaminant in ground water. Most cited example is that the ground water in inner Mongolia of China is mainly affected by As(V) [5]. Therefore, removal of As(V) is potentially important as As(III) irrespective of toxicity. Each of the available conventional technologies like coagulation/co-precipitation, adsorption on to surfaces, membrane technologies and ion exchange methods on arsenic removal [8,15–17] has some advantages and disadvantages which make the selection of a suitable method more critical. Most convenient method should have some essential requirements: simple, low-cost, high-efficiency, rural focus, based on local and easily accessible materials, etc. [5,13,18].

One promising method appears to be adsorption via ion exchange by using low-cost ion exchangers like zeolites. The use of cation exchange properties of zeolites has received considerable attraction over the past decade in water and industrial waste treatment [12,19–21]. Several zeolites like clinoptilolite, chabazite, SZP1, 13X, 5A, Y, ferrierite, ZME, ZH, synthetic mordenite, ZSM-5 and beta have been identified as potential adsorbents for arsenic removal [4,5,8,12,22–24] in addition to usual low-cost adsorbents like treated slags, char carbon and coconut husk carbon, biosorbents as well as some commercial adsorbents such as resins, gels, silica, etc. A comprehensive review on the subject may be found elsewhere [10]. The arsenic adsorption on zeolites is the result of exchange between terminal aluminol or silanol hydroxyl groups and adsorbate anionic species. When zeolite is in contact with water, terminal aluminol or silanol hydroxyl groups will develop at the edges of the zeolite particles [5,8,25].

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The synthetic zeolites are useful because of their controlled and known physicochemical properties relative to that for natural zeolites [8]. In the present work, studies are focused on evaluation of the effectiveness of the synthetic zeolites H-MFI-24 and H-MFI-90 as adsorbents for As(V) removal from model aqueous solution. The potentialities of the adsorbents are their different porous nature as well as Si/Al ratio which have great impact on arsenic removal process. Adsorption properties as a function of other operational conditions like contact time, solution pH, initial arsenic concentration, temperature, etc. have been investigated and sorption data are applied to various isotherm models in order to exploit different important sorption parameters.

## 2. Experimental

### 2.1. Zeolite adsorbents and other reagents

The synthetic zeolites H-MFI-24 and H-MFI-90 in their H-form are supplied by Süd-Chemie Catalysts Japan Inc. and used as a powder. Before use, the adsorbents are dried at 100 °C for about 12 h and stored in a desiccator. The abbreviations, surface area, Si/Al ratio, Si or Al contents with some other physicochemical properties of the zeolites are illustrated in Table 1. The Si and Al contents for H24 are not provided by the manufacturer and subsequently determined by LiBO<sub>2</sub> flux-fusion technique using ICP-AES. The analytical grade reagents like Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O, NaNO<sub>3</sub>, NaOH and HNO<sub>3</sub> are supplied by Wako Pure Chemical Industries and used without further purification.

### 2.2. Preparation of stock solutions

An aqueous solution (1000 mg L<sup>-1</sup>) of As(V) is prepared by dissolving analytical grade disodiumhydrogenarsenate, Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O into deionized water of pH 6.42, conductivity 1.01 × 10<sup>-4</sup> sm<sup>-1</sup> (Yamato, WG222 Water Purifier). The arsenic solutions used in each study are prepared by fresh appropriate dilution of this stock solution. Essentially, the concentration of arsenic species is always given as the concentration of elemental arsenic. Similarly, desired amount of 0.1 M NaNO<sub>3</sub>, 0.01 M NaOH and 0.01 M HNO<sub>3</sub> solutions are prepared at a time and stocked for use in the different experiments.

### 2.3. Instrumentation

FT-IR spectra in the range 400–4000 cm<sup>-1</sup> are recorded using Jasco 460 plus spectrophotometer in KBr disk. The good crystallinity and purity of the adsorbents are confirmed by X-ray diffraction (XRD) using a Rigaku Miniflex with Cu Kα filtered radiation (30 kV, 15 mA). The patterns are recorded in the 2θ range 5–50° with a scanning speed of 2° min<sup>-1</sup>. Pore size distributions of the adsorbents are determined from nitrogen adsorption with the Gemini,

Micromeritics instrument at 77 K. Before operation, the samples are degassed at 200 °C for 3 h under –0.1 MPa to remove any contaminants that may be present at the surface. The concentration of arsenic solutions and Si%, Al% are measured using inductively coupled plasma-atomic emission spectroscopy (Model ICPS-7500; Sequential Plasma Spectrometer; Shimadzu Corporation, Japan). Samples are collected by a syringe and filtered through a millipore 0.45 μm pore size membrane filter before analysis. Calibration standards are prepared using standard solutions certified by the supplier. Solution pH is measured with a digital pH meter of Horiba Ltd., Japan (Model D-51).

### 2.4. Sorption experiments

#### 2.4.1. Determination of pH<sub>PZC</sub>

The point of zero charge (pH<sub>PZC</sub>) is estimated by using batch equilibrium techniques. For this, 0.1 g of each adsorbent is treated with 50 mL 0.1 M NaNO<sub>3</sub> solution which is used as an inert electrolyte. The initial pH values (pH<sub>initial</sub>) are adjusted in the range ~2.5 to ~11.85 by adding minimum amounts of 0.01 M NaOH or 0.01 M HNO<sub>3</sub> solutions. The suspensions are allowed to equilibrate for 6 h in a rotary shaker fixed at 200 rpm at room temperature (r.t; 20 ± 1 °C). After completion of the equilibration time, the admixtures are filtered and final pH values (pH<sub>final</sub>) of the filtrates are measured again.

#### 2.4.2. Influence of contact time

An aliquot (50 mL) of 100 mg L<sup>-1</sup> As(V) solution is measured accurately. The pHs of the solutions are maintained at ~6.5 and ~3.2 for H24 and H90, respectively, by adding 0.01 M NaOH or 0.01 M HNO<sub>3</sub> solutions. The ionic strengths of the solutions are maintained at ~0.1 M using NaNO<sub>3</sub> solution. Afterwards, the final volumes of the solutions are made up to 0.1 L by adding deionized water and 0.1 g of each adsorbent is added to the solutions. The ultimate suspensions are shaken at 200 rpm at r.t for different time intervals ranging from 10 min to 3 h. The resulting suspensions are filtered through Whatman filter paper to achieve solid–liquid separation followed by washing with water. Finally, the volumes of the solutions are again made up to 0.2 L from which 12 mL is sucked with a syringe to filter again through a 0.45 μm membrane filter and subsequently As(V) concentrations are measured using ICP-AES.

#### 2.4.3. Influence of solution pH

The experiments are carried out by varying the initial solution pH values from ~3 to ~12 by following the same procedure and analytical technique used for the study of the influence of contact time. Accordingly, adsorption is performed by adding 0.1 g of each adsorbent to 50 mL of a 100 mg L<sup>-1</sup> As(V) solution followed by volume make up as discussed before. The final suspensions are placed in a shaker and allowed to equilibrate for 100 min for both adsorbents. It is difficult to adjust pH for an aqueous solution with zeolite as adsorbent; the experiments were performed by several repeats for one pH value.

#### 2.4.4. Influence of initial As(V) concentration

Experimental runs are carried out to assess the effect of initial As(V) concentration on adsorption by zeolites. In this case, the initial As(V) concentrations are fixed at 10, 20, 50, 100 and 150 mg L<sup>-1</sup> and experimental and analytical parts are same as explained above.

#### 2.4.5. Influence of reaction temperature

The influences of five different temperatures viz. 20, 35, 50, 60 and 70 °C on arsenic adsorption have been evaluated by using 0.1 g

**Table 1**  
Physicochemical properties of the zeolite adsorbents

Adsorbents	H-MFI-24	H-MFI-90
Abbreviation	H24	H90
Forms	H <sup>+</sup>	H <sup>+</sup>
Si (wt.%)	48	46 <sup>a</sup>
Al (wt.%)	3.9	0.98 <sup>a</sup>
Si/Al <sup>a</sup> (atomic)	12	45
pH in water	7.93	5.30
pH <sub>PZC</sub>	6.8	3.6
Surface area (m <sup>2</sup> g <sup>-1</sup> ) <sup>a</sup>	450	400
Ring size	10	10

<sup>a</sup> Information supplied by the manufacturer.

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