



## 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 as 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.

of adsorbent H24 in 50 mL of 100 mg L<sup>-1</sup> As(V) solution. The experimental and analytical parts are similar to those explained above.

#### 2.4.6. Desorption of As(V) ions

HCl (0.1 N) and NaOH (0.1 N) solutions are prepared in order to conduct desorption experiments. Following reaction to remove arsenic from solution, the zeolite (H90) is separated from solution and re-suspended for 12 h in both acid and base solutions and subsequently washed and filtered in order to regenerate the material. The zeolite is again treated with an arsenic solution (100 mg L<sup>-1</sup>) as explained earlier to evaluate the efficiency after regeneration.

#### 2.5. Adsorption performance calculations

The arsenic uptake,  $q$  (mg g<sup>-1</sup>) is calculated following the equation:  $q = (C_i - C_f)V/m$  and % adsorption =  $(C_i - C_f)100/C_i$  where  $C_i$  and  $C_f$  are the concentrations (mg L<sup>-1</sup>) of arsenic in initial and final solutions, respectively,  $V$  is the volume of the reacting solutions (L),  $m$  is the weight (g) of the adsorbents.

### 3. Results and discussion

#### 3.1. Adsorbents physicochemical properties

The zeolites H24 and H90 show similar spectral pattern in IR spectroscopy indicating structural similarity between them and necessary band interpretation is explained for H90 only. Two usual weak -OH stretching vibrational bands are observed at 3670 and 3423 cm<sup>-1</sup> due to terminal Si-OH and extra zeolitic Z-OH (also designated as Si(OH)Al) functionalities, respectively. Two low intensity bands at 1980 and 1873 cm<sup>-1</sup> are attributable to the combination band of T-O fundamental lattice ring vibration (T=Si, Al). On the other hand, the band appeared at 1630 cm<sup>-1</sup> is due to the bending mode of H<sub>2</sub>O. The peaks near about 1220 and 1075 cm<sup>-1</sup> represent the external and internal vibrations of framework TO<sub>4</sub> tetrahedra, respectively. The peak for -OTO- linkages is recorded at 802 cm<sup>-1</sup>. Two strong vibrations in the high frequency region at 546 and 449 cm<sup>-1</sup> are ascribed to T-O bending modes. These sets of IR values match closely with the reported values in literature [14,26]. Crystal structure analyses performed by X-ray diffraction (XRD) reveal a highly pure and well-crystalline nature of the zeolite adsorbents and as expected, XRD-patterns are relative to MFI framework topology. Pore size distributions and volume of N<sub>2</sub> adsorbed in the zeolites are investigated by low temperature N<sub>2</sub> adsorption with BET equipment as presented in Fig. 1. H90 is highly mesoporous in nature compared to H24. The figure reveals that H24 comprises only 2.1% pore in mesopore region of 50–60 nm while H90 is composed of 15.4% pore in the same region. In contrary, in micropore region of 1–1.5 nm, H24 consists of 27.4% pore which is too high compared to 5.5% for H90. The volume of N<sub>2</sub> adsorbed by H90 in the region of 50–60 nm is 0.055831 cm<sup>3</sup> g<sup>-1</sup> while H24 showed only 0.001024 cm<sup>3</sup> g<sup>-1</sup> adsorption in the same region.

#### 3.2. Determination of point of zero charge (pH<sub>PZC</sub>)

The pH value of adsorbent solution where the net surface charge is zero is defined as pH<sub>PZC</sub>. It has great impact in adsorption study because multivalent cation adsorption is occurred effectively at a pH below pH<sub>PZC</sub> [27]. The batch experiments are carried out using 0.1 g of each adsorbent and results are illustrated in Fig. 2. A plot of pH values of filtered solution after equilibrium (pH<sub>final</sub>) as a function of initial pH values (pH<sub>initial</sub>) provides pH<sub>PZC</sub> of the adsorbents by the common plateau of constant pH to the ordinate at around

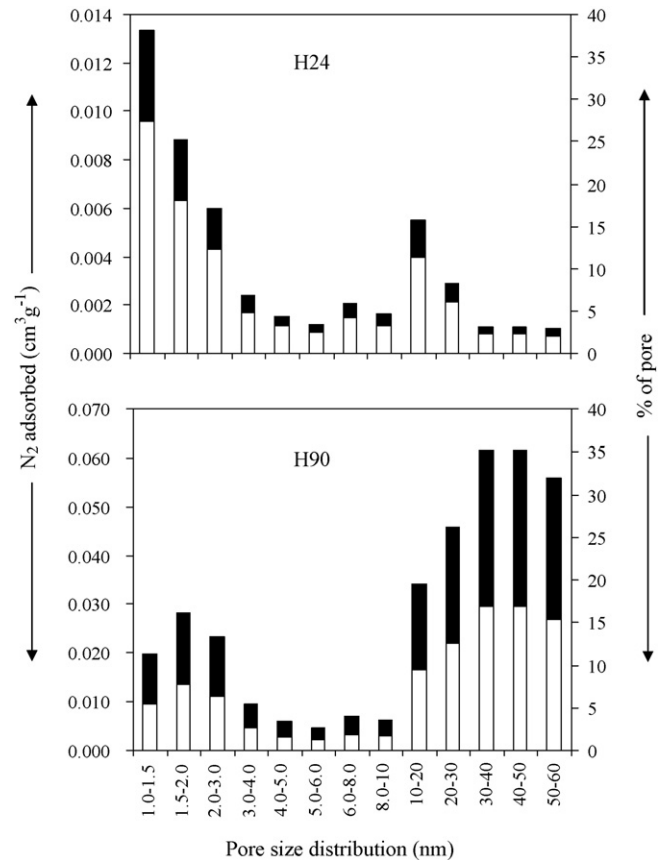


Fig. 1. Percentage of pore (□) and volume of N<sub>2</sub> adsorbed (■) in the range from 1.0 to 60 nm.

~6.8 and ~3.6 for H24 and H90, respectively (Table 1). In adsorption experiments, the respective pHs of these two adsorbent's solutions are fixed at ~6.5 and ~3.2 which are below their corresponding pH<sub>PZC</sub>. The pH<sub>PZC</sub> values of synthetic zeolite HUD (H<sup>+</sup>) and its Al<sup>3+</sup>-activated form are reported to be 6.5 and 7.5, respectively [25]. The pH<sub>PZC</sub> of adsorbents depends on various factors like nature of crystallinity, Si/Al ratio, impurity contents, temperature, sorbability of

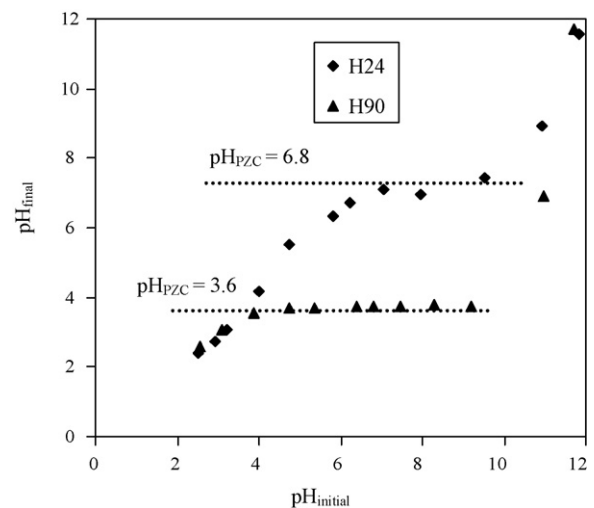
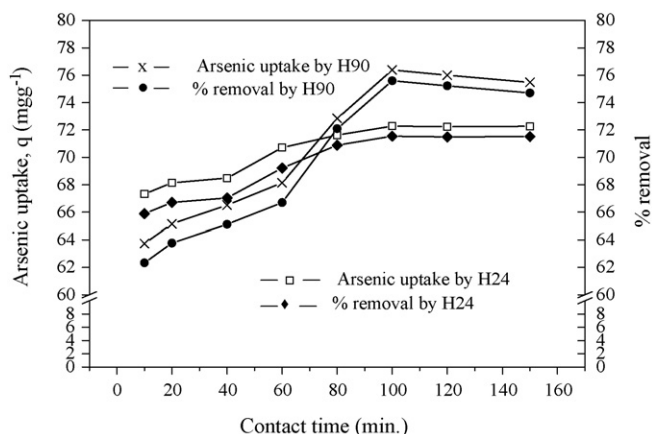


Fig. 2. Plots of pH<sub>final</sub> as a function of pH<sub>initial</sub> for the determination of pH<sub>PZC</sub> (conditions: adsorbent amount, 0.1 g; background electrolyte, 50 mL of 0.1 M NaNO<sub>3</sub>; contact temperature, r.t.; reaction time, 6 h).



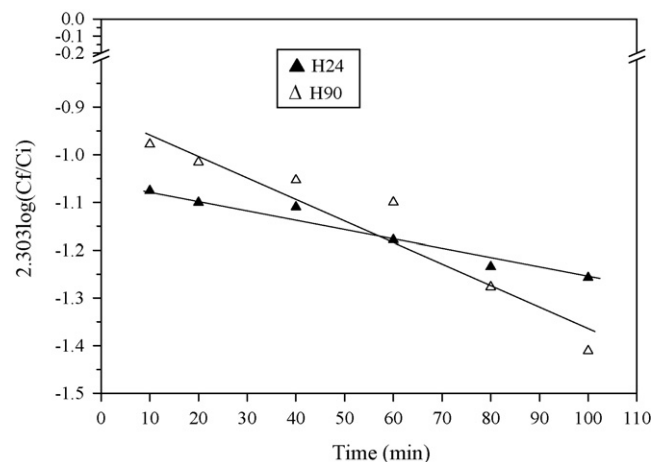
**Fig. 3.** Time dependence of As(V) adsorption on to H24 and H90 (conditions: adsorbent amount, 0.1 g; initial As(V) concentration, 100 mg L<sup>-1</sup> (50 mL); reaction temperature, r.t; pH, ~6.5 for H24 and ~3.2 for H90; background electrolyte, 0.1 M NaNO<sub>3</sub>; reacting volume, 0.1 L).

the electrolytes and degree of H<sup>+</sup> and OH<sup>-</sup> ions adsorption, and therefore may vary from adsorbent to adsorbent [28].

### 3.3. Adsorption of arsenic on synthetic zeolites

#### 3.3.1. Influence of contact time and sorption kinetics

The adsorption of arsenic is greatly dependent on contact time with adsorbent and such experiments provide equilibrium time after which adsorption could not be achieved. The experiments have been performed with 0.1 g of zeolite powder and 50 mL of 100 mg L<sup>-1</sup> As(V) solution at r.t for 10, 20, 40, 60, 80, 100, 120 and 150 min reaction time. The important findings are represented in Fig. 3 which reveals that, arsenic uptake ( $q$ ) increases with increasing contact time until the state of equilibrium is reached due to saturation of adsorbent's active sites. Over 70% of the arsenic is taken up within 80 min exposure and maximum 72.3 and 76.4% arsenic have been removed within 100 min reaction time by H24 and H90, respectively. The removal is rapid within the first 80 min, slowing down between 80 and 100 min and then gradually approaching equilibrium after 100 min for both the adsorbents. This is due to the fact that two processes may involve during adsorption, a fast ion exchange followed by chemisorption [13]. Since an increase of time to 150 min does not show any notable effects, the contact time of 100 min is chosen for both the adsorbents for further experiments. It is observed that over 60% arsenic is adsorbed by both the adsorbents at 10 min exposure. The initial arsenic uptake by both the adsorbents is high as a large number of adsorption sites are available for adsorption. In the initial bare surface, the sticking probability is large and consequently adsorption proceeds with a high rate. With the time, the active site also gradually decreases due to which the adsorption process becomes slow. The adsorption performance of the zeolites in general could be explained on the basis of Si/Al ratio in the adsorbents. Lower Si/Al ratio will be giving raise to high concentration of terminal aluminol sites. These sites play the key role [8,25] and accelerate the ion exchange process taking place during adsorption. In the present study, H90 consist of high Si/Al ratio (45) compared to that of H24 (12), still showing high performance unlike the previous results reported. This can be attributed that a factor rather than Si/Al ratio is responsible for this anomaly. During the ion exchange process, arsenic ions had to move through the pores of the zeolite mass and the diffusion will be fast through the pores of large size [2]. As illustrated in Fig. 1, adsorbent H90 is highly mesoporous in nature which could be the cause of showing more efficiency compared to H24.



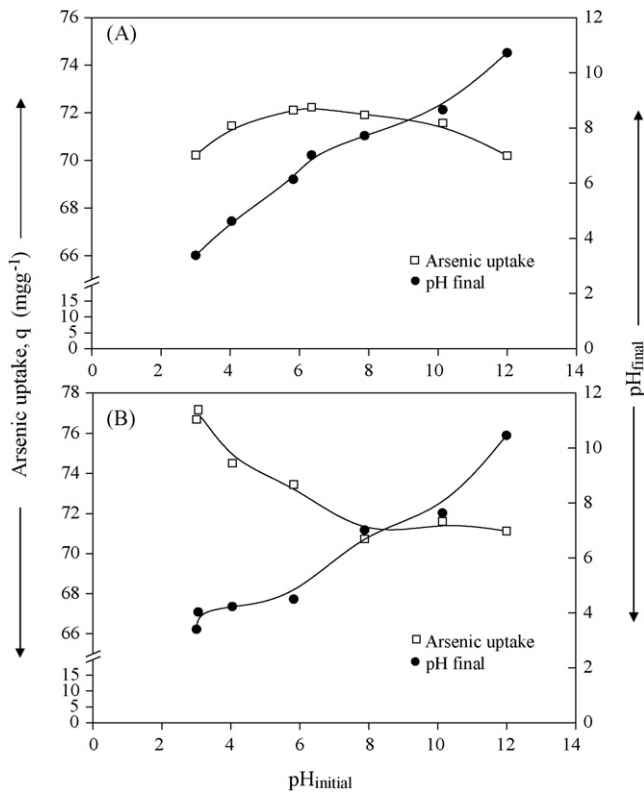
**Fig. 4.** The rate curves of the first-order kinetic model for adsorption of As(V) by H24 and H90 at r.t (conditions: adsorbent amount, 0.1 g; initial As(V) concentration, 100 mg L<sup>-1</sup> (50 mL); pH, ~6.5 for H24 and ~3.2 for H90; background electrolyte, 0.1 M NaNO<sub>3</sub>; reacting volume, 0.1 L).

Adsorption of As(V) on to H24 and H90 is found to be time dependent which follows the first-order kinetics to a significant extent, indicating that the adsorption of arsenic on to zeolites is dependent on the concentration of the reacting arsenic only. Amongst several kinetic models, first-order kinetic equation is selected based on the highest regression coefficients ( $R^2$ ) which also follows a good agreement between the model and current experimental results. The first-order rate equation can be expressed as  $\log(C_f/C_i) = -kt$  where  $C_i$  and  $C_f$  are initial As(V) concentration and concentration at time  $t$  (min), respectively, and  $k$  the rate constant (min<sup>-1</sup>). Applying the pseudo-first order condition for both the adsorbents, i.e. keeping the adsorbent concentration constant, the plot of  $\log(C_f/C_i)$  versus time,  $t$  (Fig. 4) shows a good linear fit with  $R^2$  values 0.9668 and 0.9234 for H24 and H90, respectively, during the reaction course up to equilibrium time. The respective rate constants ( $k$ ) for H24 and H90 computed from slopes of the plots are  $2.1 \times 10^{-3}$  and  $4.7 \times 10^{-3}$  min<sup>-1</sup>. The reactivity of H90 is more than two times higher than H24 due to which former deserves the more arsenic sorption capacity.

#### 3.3.2. Dependence of arsenic removal on initial pH of solution

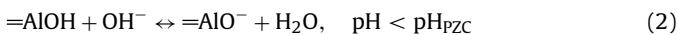
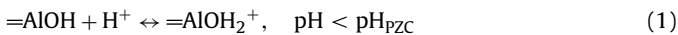
The pH is a critical criterion for determining the adsorbent's surface characteristics and the adsorption equilibrium of adsorbates. The standard range of pH in drinking water varies from 6.5 to 8.5 [9] and therefore the investigation of effect of wide range of pH on arsenic removal is needed. The adsorption of arsenic on to H24 and H90 has been conducted using the initial pH range ( $\text{pH}_{\text{initial}}$ ) ~3 to ~12. Accordingly, 0.1 g of zeolite samples are treated at r.t with 50 mL As(V) solution with concentration 100 mg L<sup>-1</sup> for 100 min at different pH values. After completion of reaction, equilibrium pH ( $\text{pH}_{\text{final}}$ ) values as well as the residual arsenic concentration,  $q$  (mg g<sup>-1</sup>) are measured and results are presented in Fig. 5. For the adsorbent H24, the  $\text{pH}_{\text{final}}$  increases smoothly with the increase of  $\text{pH}_{\text{initial}}$  (Fig. 5A). However, in case of adsorbent H90, a plateau near  $\text{pH}_{\text{PZC}}$  is found up to pH 6 and then again starts to increase with initial pH (Fig. 5B). In both the cases, arsenic uptakes increase up to near  $\text{pH}_{\text{PZC}}$  (~6.5 for H24 and ~3.2 for H90) and afterwards decrease with increase of pH. A maximum arsenic uptake of 72.2 mg g<sup>-1</sup> is estimated at pH 6.35 for H24 while H90 adsorbed maximum arsenic (77.16 mg g<sup>-1</sup>) at pH 3.15.

The reactions taking place during adsorption process depend on the predominant protonation state of surface aluminol group and the arsenate oxyanion [8]. The aluminol groups are supposed to be



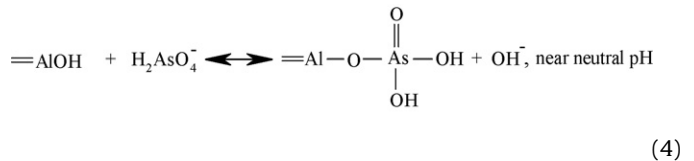
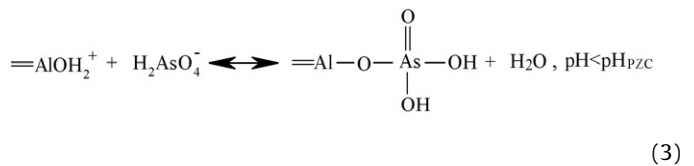
**Fig. 5.** The  $\text{pH}_{\text{final}}$  and arsenic uptake,  $q$  as a function of  $\text{pH}_{\text{initial}}$  for As(V) sorption by (A) H24 and (B) H90 at r.t. (conditions: adsorbent amount, 0.1 g; initial As(V) concentration,  $100 \text{ mg L}^{-1}$  (50 mL); contact time, 100 min; background electrolyte, 0.1 M  $\text{NaNO}_3$ ; reacting volume, 0.1 L).

reactive sites and surface silanol groups developed at the edges of zeolite particles have substantially lower adsorption capacity [29]. Eqs. (1) and (2) illustrate the surface charge property of aluminol active sites on zeolite:



where  $=\text{AlOH}$ ,  $=\text{AlOH}_2^+$  and  $=\text{AlO}^-$  are the neutral, protonated and hydroxylized aluminol sites, respectively. It could be a fact that these are just some aluminum species present on the surface of the zeolites, some other species such as  $\text{Al}(\text{OH})_3$ ,  $\text{AlOH}_2^{2+}$ ,  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$  and  $\text{Al}(\text{OH})_4^-$  may also emerge in the adsorption system [5]. As reported in previous works [5,30], two forces viz. chemical interaction and electrostatic forces play the key role in an adsorption process. The latter gives rise the Coulombic attraction or repulsion between binding sites and adsorbing ions. The  $\text{pH}_{\text{PZC}}$  values for H24 and H90 are 6.8 and 3.6, respectively, and hence at  $\text{pH} < \text{pH}_{\text{PZC}}$ , aluminol active site exists as  $\text{AlOH}_2^+$  (Eq. (1)) and  $\text{H}_2\text{AsO}_4^-$  form of arsenate will be predominant in this pH range [6,8,31]. A strong Coulombic attraction between  $\text{H}_2\text{AsO}_4^-$  and  $\text{AlOH}_2^+$  (Eq. (3)) along with chemical interaction lead to a higher arsenic uptake up to pH value less than  $\text{pH}_{\text{PZC}}$ . At initial  $\text{pH} > \text{pH}_{\text{PZC}}$ , although arsenic species is still negatively charged [6,8,31], the aluminol active sites also become negatively charged  $\text{AlO}^-$  (Eq. (2)). Consequently, arsenic uptake reduces as a result of Coulombic repulsion between active sites and existing arsenic species. As the solution pH is raised towards the neutral value particularly in case of H90 ( $\text{pH}_{\text{PZC}}$  3.6), the magnitude of Coulombic attractive force reduces as the adsorbent's active site become neutral and reactions proceed by chemical interaction involving ligand

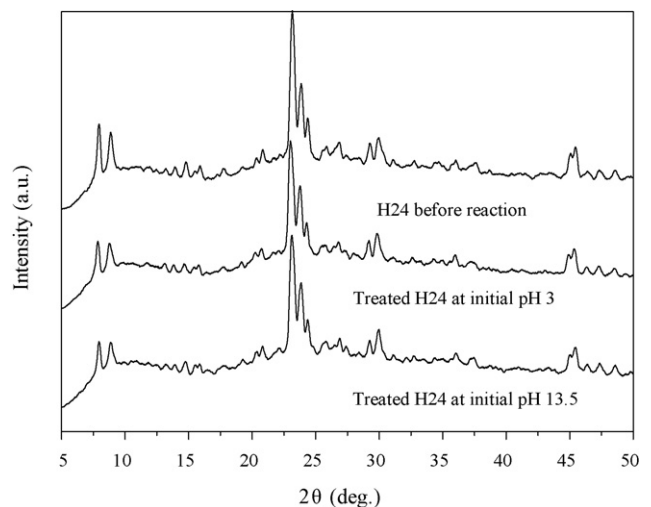
exchange dominantly (Eq. (4)). In the absence of Coulombic attraction, the quantity of arsenic adsorbed also decreases:



In order to investigate the structural variation to the zeolite materials in a wide range of pH, X-ray diffraction analyses are carried out for parent and arsenic-laden zeolites. All the optimum conditions are allowed to prepare the arsenic-laden H24 and H90. Fig. 6 shows the XRD patterns for parent and treated adsorbent H24 at pH range ~3 to ~13.5 which infer that introduction of arsenic had not affected any structural changes in the zeolite framework. The XRD patterns for H90 also give raise the same observation. Thus, zeolite structures remain intact and consequently effective for arsenic removal within the investigated pH range 3–13.5. This observation has given an additional impact to H24 and H90 over the synthetic zeolite  $\text{NH}_4^+/\text{Y}$  investigated by Shevade and Ford [8]. The structure of  $\text{NH}_4^+/\text{Y}$  became unstable at initial pH 13.2 resulting in alteration to predominantly a poorly crystalline aluminosilicate due to which arsenic removal efficiency was reduced significantly.

### 3.3.3. Influence of initial arsenic concentration

The effect of initial concentrations of 10, 20, 50, 100 and  $150 \text{ mg L}^{-1}$  on the adsorption of As(V) by H24 and H90 has been evaluated by adopting batch technique. Accordingly, 0.1 g of each zeolite is treated with 50 mL arsenic solution for a reaction period of 100 min at r.t. and solution pH are adjusted at 6.5 and 3.2 for H24 and H90, respectively. The experimental results reveal that arsenic uptake increases with decrease in initial arsenic concentration. In case of As(V) adsorption on to H90, the percent removal increases from 73.13% at  $150 \text{ mg L}^{-1}$  to 79.13% at  $10 \text{ mg L}^{-1}$ . Similarly, adsorption performance increases from 69.67% at  $150 \text{ mg L}^{-1}$  to 75.41%



**Fig. 6.** XRD patterns of the parent H24 and arsenic-laden H24 at different pH.

at 10 mg L<sup>-1</sup> while using H24 as adsorbent. At higher concentrations, some energetically less favourable sites become involved and arsenic uptake decreases with increasing arsenic concentration in the aqueous solution [2]. At lower concentrations, most of the arsenic ions present in the solution would interact with the binding sites facilitating higher adsorption.

The concentration of arsenic in fresh water varies from less than 0.05 to more than 5000 µg L<sup>-1</sup> depending on the source of arsenic, mobility and the local geographical environment [32]. It is essential to evaluate the applicability of the tested zeolites in low concentration range (in ppb) where we face the arsenic problem in drinking water. Therefore, initial As(V) concentration is further decreased and experiments have also been carried out with initial As(V) concentrations of 0.5 and 2 mg L<sup>-1</sup> keeping the other conditions same. The adsorption of arsenic with concentration 2 mg L<sup>-1</sup> on to adsorbent H90 reveals that the aqueous phase arsenic concentration decreases to 0.048 mg L<sup>-1</sup> after 80 min, resulting in less than 0.036 mg L<sup>-1</sup> at 100 min equilibrium time. The aqueous phase arsenic concentration at equilibrium time is 0.025 mg L<sup>-1</sup> while using 0.5 mg L<sup>-1</sup> As(V) solution. The adsorption ability of the H24 is still low compared to H90 and residual arsenic concentrations are 0.055 and 0.041 mg L<sup>-1</sup> while using 2 and 0.5 mg L<sup>-1</sup> initial arsenic concentrations, respectively. Further decrease of initial concentration has no influence on the removal performance of the adsorbents. The saturation of binding sites may be due to the fact that zeolites minerals are heterogeneous in nature with regards to the binding sites. All sites are not equally active for adsorbing species. However, it is worth to mention that the tested zeolites are efficient to remove arsenic from both high- and low-concentration ranges. The adsorbents H24 and H90 even reduce arsenic concentration below the WHO's earlier guideline value of 0.05 mg L<sup>-1</sup> As in drinking water. These observations have a good correlation with the previous report [8] where NH<sub>4</sub><sup>+</sup>/Y reduced arsenic concentration below 33 ppb while using 5 ppm initial solution. Essentially, the present results are promising for the use of H24 and H90 to treat contaminated drinking water where arsenic is at very low concentrations.

The present investigation is mainly dealt with the removal of As(V) and therefore a model aqueous solution enriched in As(V) is used in the experiments so that influence of other metals that may present in the solution could be nominal. The tested adsorbents remove arsenic from both ppm and ppb levels of initial concentrations which prompt us to conclude that the zeolites H24 and H90 are efficient in removing As(V) even in the presence of some light metals like calcium, magnesium, sodium and iron in trace amounts in the investigated model solution which is evidenced from ICP-AES.

### 3.3.4. Influence of reaction temperature

The effect of five different temperatures viz. 20, 35, 50, 60 and 70 °C on arsenic adsorption by H24 is investigated. For the purpose, 0.1 g H24 powder and 50 mL of 100 mg L<sup>-1</sup> As(V) solution are kept in contact for 100 min at the above-mentioned temperatures. In the range between 20 and 50 °C, temperature has only marginal effect (not reportable) on the adsorption performance of the zeolite. Because of that, temperature is increased even up to 70 °C so that a particular trend could be gained in order to define whether the adsorption is exothermic or endothermic in nature keeping aside the fact that it will be not happening in real life systems. The adsorption affinity is marginally decreased from 73.73 mg g<sup>-1</sup> at 20 °C to 72.9 mg g<sup>-1</sup> at 70 °C. This observation provides an indication about the exothermic nature of the adsorption process [33] due to which the rise of temperature suppresses the adsorption affinity. Unlike to the present study, adsorption of arsenic on natural zeolites reported by Menhage-Bena et al. [9] was found to be temperature dependent

and adsorption performance was increased with increase in temperature. In consistent with the present results, Borah and Senapati [27] reported that adsorption of Cd(II) on to pyrite surface decreased with increase in temperature. There is no particular trend of metal uptake which could be due to fact that temperature changes can alter several factors like rate of adsorption, hydrolysis, recrystallization reactions and dissociation constants of water. Combined effects of these entire factors marginally degrade the adsorption performance in support of the present study.

### 3.3.5. Adsorption isotherms

The equilibrium data obtained from the adsorption of arsenic on to H24 and H90 over the initial arsenic concentration ranging from 10 to 150 mg L<sup>-1</sup> previously discussed in Section 3.3.3 are correlated with the Langmuir monolayer isotherm model [34]. The model is based on some assumptions which include metal ions are chemically adsorbed at a fixed number of well-defined sites, each site can hold only one ion, all sites are energetically equivalent and there is no interaction between the ions, etc. [34]. The Langmuir linearized isotherm is given by the following equation:

$$\frac{C_f}{Q} = \frac{1}{Q_{\max}B} + \frac{C_f}{Q_{\max}}$$

where  $Q$  is milligrams of arsenic adsorbed per gram of the adsorbent,  $C_f$  is arsenic concentration in final solutions (mg L<sup>-1</sup>),  $Q_{\max}$  (g g<sup>-1</sup>) and  $B$  (L g<sup>-1</sup>) are Langmuir constants related to sorption capacity and sorption energy, respectively. Maximum sorption capacity denoted by  $Q_{\max}$  represents monolayer coverage of sorbent with sorbate and  $B$  implies the enthalpy of sorption which should vary with temperature. A good linear plot (figure omitted for sake of brevity) is obtained by plotting  $C_f/Q$  against  $C_f$  for both H24 and H90 over the entire range of arsenic concentration investigated. Langmuir parameters together with regression coefficients determined from the plot (Table 2) confirm a good agreement between theoretical model and experimental result obtained.  $Q_{\max}$  values computed from slopes of plots are 0.0358 and 0.0348 g g<sup>-1</sup> for H24 and H90, respectively, while their respective  $B$  values derived from intercepts are 9.04 and 10.87 L g<sup>-1</sup>. The deviation from Langmuir isotherm at lower concentrations observed for H24 is due to active site saturation by adsorbate species.

If the number of adsorption sites is large relative to the number of contaminant molecules, the Freundlich isotherm model could be apply to the sorption system which describes the physical sorption of sorbate only. In contrast to the Langmuir monolayer model, Freundlich isotherm is a consecutive layer model which does not predict any saturation of the sorbent by sorbate [35]. The linearized form of Freundlich isotherm (Eq. (5)) used to evaluate the different sorption parameters (Table 2) represents the best suit to the present

**Table 2**  
Summary of equilibrium isotherm parameters for As(V) uptake by H24 and H90

Isotherm models	Parameters			R <sup>2</sup>
	Langmuir			
	Q <sub>max</sub> (g g <sup>-1</sup> )	B (L g <sup>-1</sup> )		
H24	0.0358	9.04		0.9566
H90	0.0348	10.87		0.9642
Freundlich	K <sub>f</sub> (mg g <sup>-1</sup> )	n	−ΔG (kJ mol <sup>-1</sup> )	R <sup>2</sup>
	H24	3.52	1.11	19.89
H90	4.21	1.12	20.33	0.9993
DKR	β (mol <sup>2</sup> J <sup>-2</sup> )		E (kJ mol <sup>-1</sup> )	R <sup>2</sup>
	H24	−8.6 × 10 <sup>-9</sup>		8.12
H90	−8.3 × 10 <sup>-9</sup>		8.27	0.9993

**Table 3**  
Comparison of adsorption performance of tested adsorbents with previous works

Adsorbents	As concentration	Si/Al	% removal	Capacity (isotherm)	Ref.
NH <sub>4</sub> <sup>+</sup> -Y (commercially available zeolite)	5 mg L <sup>-1</sup>	6	>99	–	[8]
NH <sub>4</sub> <sup>+</sup> -ferrierite, NH <sub>4</sub> <sup>+</sup> -ZSM-5, H <sup>+</sup> -Y (commercially available zeolites)	5 mg L <sup>-1</sup>	–	Not effective	–	[8]
SZFe (Fe-treated synthetic zeolite)	2 × 10 <sup>-3</sup> mol L <sup>-1</sup>	–	>99	22.50 mg g <sup>-1</sup> (experimental)	[32]
CeZP (cerium(III) exchange synthetic zeolite)	40 mg L <sup>-1</sup>	–	–	23.42 mg g <sup>-1</sup> (Langmuir)	[39]
Al-zeolite (aluminum(III) exchange synthetic zeolite)	1.3 mM	–	–	10.50 mg g <sup>-1</sup> (Freundlich)	[5]
H-MFI-24	10 mg L <sup>-1</sup>	12	>76	35.80 mg g <sup>-1</sup> (Langmuir)	Current research
H-MFI-90	10 mg L <sup>-1</sup>	45	>80	34.80 mg g <sup>-1</sup> (Langmuir)	Current research
Coconut shell carbon with 3% ash (commercial activated carbon)	0–200 mg L <sup>-1</sup>	–	–	2.40 mg g <sup>-1</sup> (Langmuir)	[40]
Activated carbon produced from oat hulls (synthetic activated carbon)	25–200 μg L <sup>-1</sup>	–	–	3.08 mg g <sup>-1</sup> (Langmuir)	[41]

data points:

$$\ln Q = \ln K_F + \frac{1}{n} \ln C_f \quad (5)$$

This isotherm is usually used in special cases for heterogeneous surface energy where it is characterized by the heterogeneity factor  $1/n$ . The parameter  $Q$  denotes the equilibrium value of arsenic adsorbed per unit weight of synthetic zeolite powder (mg g<sup>-1</sup>),  $C_f$  implies the liquid-phase sorbate concentration at equilibrium (mg L<sup>-1</sup>) and  $K_F$  is the Freundlich constant (mg g<sup>-1</sup>). The  $K_F$  and  $n$  are calculated from the intercepts and slopes of the Freundlich plots of  $\log Q$  against  $\log C_f$  (figure omitted for sake of brevity). The  $K_F$  values for H24 and H90 are 3.52 and 4.21 mg g<sup>-1</sup>, respectively, while their respective  $n$  values 1.11 and 1.12 are within the range between 1 and 10 showing beneficial adsorptions [36]. The numerical value of  $0 < 1/n < 1$  (in present case  $1/n = 0.9009$  and 0.8928 for H24 and H90, respectively) indicates an adsorption process that only slightly suppressed at lower equilibrium concentrations [2] and is attributed to a heterogeneous nature of the adsorbent's surface without any interaction between adsorbed atoms, molecules or ions [37]. Knowing the  $K_F$  value, one can calculate free energy change ( $\Delta G$ ) of arsenic adsorption on to zeolite using the equation:  $\Delta G = -RT \ln(K_F \times 1000)$  where  $R$  is the gas constant (0.00831447 kJ K<sup>-1</sup> mol<sup>-1</sup>) and  $T$  is the temperature (293 K). The negative free energy values (Table 2) indicate the feasibility of the process and the spontaneous nature of adsorption.

Dubinin–Kaganer–Radushkevich (DKR) equation is based on the heterogeneous surface of the adsorbent which could be expressed as  $\ln Q = \ln X_m - \beta \varepsilon^2$  where  $Q$  is the amount of arsenic ions adsorbed per unit weight of adsorbent (mg g<sup>-1</sup>),  $X_m$  is the maximum sorption capacity (mol g<sup>-1</sup>),  $\beta$  is the activity coefficient (mol<sup>2</sup> J<sup>-2</sup>) related to mean sorption energy and  $\varepsilon$  is the Polanyi potential which can be calculated using the equation,  $\varepsilon = RT \ln(1 + 1/C_f)$  where  $R$  is the gas constant (0.00831447 kJ K<sup>-1</sup> mol<sup>-1</sup>),  $T$  is the temperature (293 K) and  $C_f$  implies the liquid-phase sorbate concentration at equilibrium (mg L<sup>-1</sup>). The slopes of the plot of  $\ln Q$  versus  $\varepsilon^2$  (not shown) provide  $\beta$  value as listed in Table 2 and intercepts yield  $X_m$ . The  $X_m$  values are unreliably large indicating inconsistency with the present study. Large values of  $X_m$  were also observed by previous workers which are probably due to the shape of the isotherms and basic principles involved in the mathematical derivation of the model [25,38]. In order to evaluate the nature of interaction between arsenic and the binding sites, the mean energy of sorption,  $E$  is also calculated (Table 2) from the relationship:  $E = 1/\sqrt{-2\beta}$ . The calculated  $E$  values for H24 and H90 are 8.12 and 8.27 kJ mol<sup>-1</sup>, respectively, which lie in the range of energies (8–16 kJ mol<sup>-1</sup>) characteristics for the ion exchange mechanisms [2,25,38].

### 3.3.6. Regeneration of the adsorbents

Preliminary regeneration experiments have been carried out using the adsorbent H90. As illustrated in Fig. 5, low adsorption of As(V) is presented in basic pH range which implies that adsorbed

arsenic can be desorbed effectively from H90 in basic medium. For convenience, desorption tests are performed using NaOH (0.1 N) and HCl (0.1 N) regeneration solutions. After desorption operation in acidic medium, 23.8% sequestered arsenic is recovered and arsenic removal capacity of the regenerate material is almost same (74.1%) with the fresh material (76.4%) while using 100 mg L<sup>-1</sup> initial As(V) solution. In base regeneration with NaOH, 45.3% of the sequestered arsenic is recovered at the cost of decrease of arsenic removal capacity of the regenerate material significantly to 21.4%. This result is consistent with the observed decrease of arsenic removal performance by H90 at basic pH range. The basic condition should be neglected while designing more efficient solutions for zeolite regeneration due to significant lost of arsenic removal capacity of the regenerate material. The arsenic-laden zeolites have passed EPA's Toxicity Characteristic Leaching Procedure test and can be safely disposed of as non-hazardous waste [9].

## 4. Conclusions

H24 and H90 zeolites are very effective adsorbents for arsenic removal from both high and low initial concentration levels. Both adsorbents reduce arsenic concentration below the WHO's earlier guideline value of 0.05 mg L<sup>-1</sup> As in drinking water. Table 3 summarizes a comparative evaluation of the investigated zeolites with some commercially available and synthetic zeolites along with some commercially available and synthetic activated carbons. In fact, evaluation is a critical task as the efficiency depends on different factors which include adsorbent dose, solution pH, contact time, initial arsenic concentration and other solution conditions. Therefore, comparison has been made in terms of most essential parameters, i.e. % removal and maximum adsorption capacity from isotherm model used. The most important observation is that tested zeolites H24 and H90 exhibit higher adsorption capacity derived from Langmuir isotherm model than most of the commercial and synthetic zeolites or activated carbons reported earlier. Essentially, the present results are promising for the use of synthetic zeolites to treat contaminated drinking water where arsenic is at very low concentrations. Moreover, the investigated adsorbents may be used in the design and performance of a fixed-bed adsorber for As(V). Activated carbon has been widely used for the removal of organic substances such as humic acid due to its extended surface area and micro- or mesoporous structure. In contrast, both synthetic and commercial activated carbons have proved to have a low arsenic uptake capacity in the ranges from 1 to 4 mg g<sup>-1</sup> only. The low adsorption capacity and relatively high-cost preclude the activated carbons from acting as a favourable adsorbent for arsenic adsorption. Consequently, the tested materials may be good substitutes for the use of activated carbon as adsorbent for arsenic.

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