Studies on the removal of As(III) and As(V) through their adsorption onto granular activated carbon/MnFe2O4 composite: isotherm studies and error analysis

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ABSTRACT
The granular activated carbon/MnFe₂O₄ composite with a mass ratio of 2:1 was synthesized using a simple chemical coprecipitation procedure and used for the removal of As(III) and As(V) from synthetically prepared wastewater. Physicochemical analysis of the composite was carried out through Brunauer, Emmett and Teller surface area and total pore volume, Fourier Transform Infrared Spectroscopy (FT-IR) and Scanning Electron Micrograph and Energy-Dispersive X-Ray Spectroscopy (SEM-EDX). The impact of various adsorption parameters such as the initial pH, adsorbent dose, contact time, temperature and initial arsenic concentration were systematically investigated to evaluate the optimum operating conditions. Nonlinear regression analysis was employed to identify the best-fit isotherm on the basis of three correlation coefficients and three error functions and also to predict the parameters involved in one one-parameter, six two-parameter, nineteen three-parameter, three four-parameter and one five-parameter isotherms. The maximum adsorption capacities estimated using the Langmuir model were 1253 mg/g for As(III) and 1314 mg/g for As(V) at 30 °C temperature and 70 min contact time. The results showed that As(III) and As(V) removal was strongly pH-dependent with an optimum pH value of 7.0 and 4.0, respectively. The mean adsorption energy (E) calculated from the D–R model indicated the nature of adsorption being ion exchange type.

1. Introduction
Arsenic is relatively scarce but ubiquitous element ranks 20th among the elements in natural abundance, 14th in seawater in addition 12th in human body. It occupies nearly 0.00005% of the entire earth's surface.[1] Billions of people are affected by poisonous effect of arsenic in various regions of world.[1,2] Arsenic is relegated as a category 1 and group A human carcinogen by the International Association For Research on Cancer and the US Environmental Protection Agency, respectively.[3] The major early impact because of acute arsenic poisoning involves dysphasia, projectile vomiting, burning and dryness of the throat and mouth, profuse diarrhoea, colicky abnormal pain and haematuria. Manifestation due to subacute
arsenic toxicity basically includes the gastrointestinal, nervous, respiratory cardiovascular and hematopoietic systems.[4] On the basis of investigation of the fatal effect of arsenic on human body, in drinking water the maximum contaminant level of arsenic has been revised to 10 μg/L from 50 μg/L by the World Health Organization in 1993 [5] and the European Commission in 2003.[6]

The sources of arsenic contamination in natural water are shown in Figure 1.[1,7] Copper smelting causes a huge volume of wastewater having large amounts of arsenic species (Table 1).
[8] With the aim of maintaining a good quality of fresh water resources, this wastewater must be treated so that the water can be reverted to the ecosystems.

Arsenic exists in both organic and inorganic forms in nature; though the organic form is unusual. Inorganic arsenic is typically found in natural water systems. The most common in natural water are As(III) and As(V).[9] Inorganic arsenic species are about 100 times more harmful than organic arsenic species and As(III) is about 60 times more harmful than As(V).[4]

Various physicochemical techniques are demonstrated to scavenge arsenic from both water and wastewater. The conventional methods used to remove arsenic are membrane techniques, oxidation/precipitation, ion exchange, electrocoagulation and adsorption.[1,7,10–13] However, these methods suffer from various drawbacks such as inadequate removal of metal, high capital and high operational cost or discarding the remaining metal sludge, energy requirements and are inappropriate for small-scale industries.[14,15] Adsorption processes are efficient practices and they have long been applied in industries to remediate inorganic and organic pollution for low cost, easy treatment, minimal sludge generation, its regeneration ability, etc.[16] Modification of surface of adsorbents is fetching a current investigation area for the expansion of low-cost arsenic scavenging technique. Zhang et al. [17] reported that bimetal oxide magnetic nanomaterials (MnFe₂O₄ and CoFe₂O₄) were synthesized and characterized and used for scavenging of As(III) and As(V). Parsons et al. [18] reported the capability of the Fe₃O₄, Mn₃O₄ and MnFe₂O₄ nanophases for scavenging As(III) and As(V) from aqueous solutions.

MnFe₂O₄, a familiar soft material, has outstanding chemical stability and frequently controls the concentration of free metal and organic matter in water or soil through adsorption reactions.[19,20] Granular activated carbon (GAC) can also remove arsenic, but to increase the adsorption capacity of GAC, it was modified with MnFe₂O₄. So Granular activated carbon/MnFe₂O₄ composite (MGAC) having the benefits of desired adsorption capacity could be used as an economical and promising adsorbent for removing a wide range of arsenic. Conversely to our best knowledge, nothing is known about effectiveness of GAC/MnFe₂O₄ composite in arsenic removal from water.

The aim of the present research was divided into two parts. First part of the study was (1) to prepare GAC/MnFe₂O₄ composite which was composed of acid treated GAC and MnFe₂O₄ via a facile coprecipitation method, (2) to characterize the prepared GAC/MnFe₂O₄ composites by various techniques, (3) formerly to study its potential in the scavenging of As(III) and As(V) from wastewater by optimizing initial pH of the solution, adsorbent dose, contact time, temperature and initial arsenic concentration, (4) discuss the probable adsorption mechanism at GAC/MnFe₂O₄ composite – solution interface, (5) after that to investigate the effect of co-existing ions present in copper smelting wastewater and (6) then to examine the adsorption and desorption behaviours of arsenic on the adsorbent.

The second part of the present research was to study 30 adsorption isotherms for adsorption of both As(III) and As(V) onto GAC/MnFe₂O₄ composite to examine their capability for modelling the adsorption equilibrium data.

2. Materials and methods

2.1. Materials

All the chemicals and reagents were of analytical reagent grade, purchased from Himedia Laboratories Pvt. Ltd., Mumbai, India and used without additional purification. Standards,
matrix modifier and wash solutions were prepared by deionized double-distilled water. The stock solutions of As(III) and As(V) were prepared by dissolving NaAsO$_2$ and Na$_2$HAsO$_4$, $7H_2$O, purchased from Himedia Laboratories Pvt. Ltd., Mumbai India, in double-distilled water, respectively.

### 2.2. Preparation of GAC/MnFe$_2$O$_4$ composite (MGAC)

GAC was washed thoroughly with double-distilled water and oven dried at 105 $^\circ$C for 4 h. Twenty five grams of dried GAC was added into 500-mL conical flask containing 250 mL of 0.5-M HCl solution; thereafter was shaken for 4 h at 120 rpm at 25 $^\circ$C. Then the mixture was left overnight. The mixture then was filtered to separate GAC which were repeatedly washed with double-distilled water to provide neutral pH. Then the adsorbents were dried at 110 $^\circ$C for 3 h for removing moisture, cooled to room temperature and kept in plastic bags for further usage.

GAC/MnFe$_2$O$_4$ composites were prepared by chemical coprecipitation method with a few modifications.\[21\] In this procedure, a fixed quantity of acid-treated GAC was mixed into 200-mL solution containing dissolved ferric (III) chloride (FeCl$_3$) (0.05 mol) and manganese (II) chloride (MnCl$_2$) (0.025 mol) at room temperature. The quantity of acid-treated GAC was fixed for acquiring GAC/MnFe$_2$O$_4$ mass ratio of 2:1. The solution temperature was increased to 60 $^\circ$C under energetic magnetic stirring and after that 5 mol/L of NaOH solution was added drop by drop to the above mixture till the pH of the solution attained 11. Thereafter, next 1 h agitation was carried on. Then the suspension was heated in a water bath at 100 $^\circ$C for 4 h. After cooling, the prepared composite was constantly washed with double-distilled water for eliminating the contaminations (e.g. Na$^+$, Cl$^-$) accompanied with the processes. Afterwards, as-prepared composite was collected from the washed solution by

![Figure 2. Outline of coprecipitation method for the preparation of GAC/MnFe$_2$O$_4$ composite.](image-url)
filtering the mixture and then was oven dried at 110 °C. Figure 2 represents the schematic diagram for the preparation of composite adsorbent. The reaction ionic equation [22] is as follows:

\[
\text{Mn}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Mn(OH)}_2 \downarrow + 2\text{Fe(OH)}_3 \downarrow \rightarrow \text{MnFe}_2\text{O}_4 + 4\text{H}_2\text{O} \quad (1)
\]

\[
\text{MnFe}_2\text{O}_4 + \text{GAC} \rightarrow \text{GAC/MnFe}_2\text{O}_4 \quad (2)
\]

### 2.3. Characterization

The physicochemical characteristics of GAC and GAC/MnFe₂O₄ composite were determined using ASTM standard procedures. Measurement of the Brunauer, Emmett and Teller (BET) surface area and total pore volume of the GAC and GAC/MnFe₂O₄ composite were done by physisorption using surface area analyzer (Micrometrics chemisorb 2720, USA) where N₂ gas was used as adsorbate.

FT-IR spectroscopy of the composite was performed using an FT-IR spectrophotometer (NICHOLET 6700, coupled with OMNIC software version 6.2) to know the functional groups present in the GAC/MnFe₂O₄ composite before and after adsorption since the extent of adsorption depends greatly on surface characteristics of adsorbent. The pellet to be analysed was obtained by compressing a mixture of sample and potassium bromide (KBr) in a ratio of 1:10 in hydraulic press at 15 ton pressure for 30 s. Pellets of biosorbent were made with KBR and spectra found in the range of 400–4000 cm⁻¹ were analysed.

The measurements of SEM were done for observing the surface morphologies of the GAC/MnFe₂O₄ composite composite (SEM; LEO electron Microscopy, England). For sample analysis, 1-mg sample was mounted on an aluminium stub and gold coating was performed via sputtering coater S150, at a pressure of 667 × 10⁻⁴ Pa for 50–60 s. Sputtering is conducted to provide conductivity to the metal surface. The images were taken with an accelerator voltage = 15 kV and an emission current = 100 μA by the Tungsten filament. EDAX analysis was also carried out to identify the presence of metal ions on the surface of adsorbent.

### 2.4. Batch experimental studies and analytical methods

Batch adsorption studies were conducted to optimize pH, adsorbent dose, contact time, temperature and initial adsorbate (As(III) or As(V)) concentration. To adjust the initial pH of the solution using a digital pH meter (HACH® India), 1.0 N NaOH and 1.0 N HCl solutions were used. The flasks were moderately shaken in an incubator cum orbital shaker (REMI Laboratory instruments) operating at 120 rpm. The standard experimental conditions for the batch adsorption experiments are given in Table 2.

The samples were withdrawn from the flasks through filtration by Whatman Filter paper (Cat No 1001 125) at predetermined time intervals for studying the effect of parameters and at equilibrium time for isotherm studies, a portion of filtrate was diluted with HNO₃ solution (10%, v/v). The filtrate was analysed for the determination of arsenic concentration using ThermoFisher Scientific iCE 3000 Series AA graphite furnace atomic absorption spectrometer (detection limit 20–100 μg/L) following the procedure reported by Singh and Pant [23] and Michon et al. [24].
With the purpose of estimating adsorption capacity, expressed as the amount of adsorbate molecules adsorbed per unit mass of adsorbent (mg/g), the adsorption capacity was calculated as follows:

\[ q_e = \frac{(C_0 - C_e) \cdot V}{M} \]  

(3)

The amount of adsorbate molecules adsorbed in terms of percentage was calculated as follows:

\[ R_e(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \]  

(4)

2.5. Interference studies

The As(III) and As(V) binding capacity experiments were further conducted with synthetically prepared wastewater containing the co-existing ions usually present in copper smelting wastewater with arsenic solution. The effect of ions such as Cu\(^{2+}\), Zn\(^{2+}\) and SO\(_4^{2-}\) (100–2000 mg/L), Fe\(^{3+}\), Cd\(^{2+}\) and Bi\(^{3+}\) (10–500 mg/L), Pb\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\) and Cr\(^{6+}\) (1–70 mg/L) on scavenging of As(III) and As(V) were inspected.

2.6. Desorption studies

The adsorption–desorption study was conducted with As(III) and As(V) ions. The adsorption study was performed following the similar procedure mentioned above. On the other hand, desorption was studied as follows: 0.1 g of the arsenic-laden GAC/MnFe\(_2\)O\(_4\) composite adsorbent from the previous metal adsorption study was added into a 250-mL round bottom flask containing 100 mL of different concentrations of NaOH (0, 0.001, 0.01, 0.05, 0.1, 0.5 and 1 M). The mixture was then agitated with the incubator cum orbital shaker at 120 rpm for 70 min at 30 °C. Then the suspension solutions were filtered and analysed for As(III) and As(V) according to the method discussed earlier. After the desorption experiment, the quantity of desorbed As(III) and As(V) was calculated by the residual As(III) and As(V) concentrations in the solution. The amounts desorbed of adsorbate were estimated using the following equation:

\[ \% \text{ Desorption} = \frac{\text{Released adsorbate (mg/L)}}{\text{Initially adsorbate adsorbed (mg/L)}} \times 100 \]  

(5)
3. Theoretical background

3.1. Isotherm studies

The capacity of the adsorption isotherm is essential and takes a governing part to determine the maximum capacity of adsorption. Mainly, it is a vital curve which defines the phenomenon that leading the retaining/discharge or movement of an adsorbate from liquid phase to solid adsorbent surface at a constant pH and temperature. It also offers a view of the process taken by the system under the study in a brief form, signifying how competently an adsorbent will adsorb and permits an estimation of the financial feasibility of the adsorbent, commercial applications for the definite adsorbent. When adsorbents containing solution has been kept in contact with the adsorbate for enough contact time and the concentration of adsorbate in the solution becomes constant, then adsorption equilibrium is achieved. Obviously, the statistical correlation playing a significant role in the isotherm modelling, operative designing and significant exercise of the adsorption systems, is observed by graphical representation of the uptake capacity of adsorbent against residual concentration of adsorbate. It is essential to form the utmost suitable correlation for equilibrium data with model predictions for optimizing the design for arsenic adsorption onto the adsorbent. Several models were proposed for describing adsorption equilibrium (The details of isotherm models provided with supplementary material).

3.2. Determining adsorption isotherm parameters by nonlinear regression

The isotherm parameter sets are calculated by the nonlinear regression owing to the inherent bias resulting after linearization. This offers a mathematically laborious method to estimate isotherm parameters using the original isotherm equation.[25–27] Mostly, Gauss–Newton methods or Levenberg–Marquardt-based algorithms [28,29] are used. As nonlinear equations, the linearization step of the isotherm models leads to the modification of the distribution of error after converting the data to a linear form.[26] The equilibrium data for adsorption of arsenic on GAC/MnFe₂O₄ composite were analysed by nonlinear curve fitting analysis using professional graphics software package OriginPro (8.5.1 version) for fitting the one, two, three, four and five-parameter isotherm models (The details are provided with supplementary material with Table S1).

The optimization method needs the choice of a goodness-of-fit measure (GoFM) with the purpose of estimating the fitting of the isotherm to the experimental data. In the present research, six GoFM (Residual sum of squares (SSE), Reduced chi-square test (Reduced $\chi^2$), coefficient of determination ($R^2$) and adjusted $R$-square ($\bar{R}^2$), $R$ value ($R$) and root-MSE value) were employed for estimating isotherm parameters using the OriginPro software by considering 95% confidence interval. (The details are provided with supplementary material.)

4. Results and discussion

4.1. Characterization

4.1.1. BET surface area and total pore volume

The BET surface area and total pore volume of the acid-treated GAC and the prepared GAC/MnFe₂O₄ composites are listed in Table 3. Conversely, while the MnFe₂O₄ was mixed with
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GAC to prepare the composite, its surface area and total pore volume decreased evidently, in comparison to that of the acid-treated GAC. This may be because of the \textit{in situ}–generated MnFe\textsubscript{2}O\textsubscript{4} covered partially the GAC surface. The BET surface area of GAC/MnFe\textsubscript{2}O\textsubscript{4} composite was much higher than that of MnZn–ferrite (2.86 m\textsuperscript{2}/g) reported by Skołyszewska et al. [30].

### 4.1.2. FT-IR analysis

The adsorption capacity of heavy metal on various adsorbents depends on the existence of various active functional groups onto the surface of adsorbent. The Fourier transform infrared spectra (FT-IR) study of unloaded as well as metal-loaded GAC/MnFe\textsubscript{2}O\textsubscript{4} composite at optimized batch experimental condition were investigated for detecting the function groups responsible mainly for the process of adsorption (Figure 3). Table 4 indicates the wavenumber for the various functional groups existing in the unloaded GAC/MnFe\textsubscript{2}O\textsubscript{4} composite and As(III)- and As(V)-loaded adsorbent. Surface –OH and –NH groups were main active functional groups responsible for As(III) and As(V) adsorption as the wavenumber shifted from 3426 cm\textsuperscript{-1} to 3442 cm\textsuperscript{-1} (As(III)) and to 3499 cm\textsuperscript{-1} (As(V)).[31] Some researchers have also reported that after the adsorption arsenic on the Fe–Ce and Fe–Mn adsorbents, the peak of hydroxyl groups reduced or vanished.[32,33] Aliphatic C–H stretching may be responsible for the adsorption of As(III) and As(V) onto GAC/MnFe\textsubscript{2}O\textsubscript{4} composite as wavenumber shifted from 2924 cm\textsuperscript{-1} to 2914 cm\textsuperscript{-1} and to 2945 cm\textsuperscript{-1}, respectively. Peak observed at 1750 cm\textsuperscript{-1} is the stretching vibration of C=O bond due to nonionic carboxyl groups (–COOH, –COOCH\textsubscript{3}), and may be assigned to carboxylic acids or their esters.

### Table 3. Properties of GAC and MGAC.

| Adsorbent                  | BET surface area (m\textsuperscript{2}/g) | Total pore volume (m\textsuperscript{3}/g) |
|----------------------------|-------------------------------------------|--------------------------------------------|
| Acid-treated GAC           | 113.537                                   | 0.057                                      |
| GAC/MnFe\textsubscript{2}O\textsubscript{4} composite | 43.393                                   | 0.022                                      |

\textbf{Figure 3.} FT-IR spectra of GAC/MnFe\textsubscript{2}O\textsubscript{4} composite (MGAC) before adsorption, GAC/MnFe\textsubscript{2}O\textsubscript{4} composite after As(III) adsorption (MGAC–As(III)) and GAC/MnFe\textsubscript{2}O\textsubscript{4} composite after As(V) adsorption (MGAC–As(V)).
Table 4 shows the responsibility of aliphatic acid C=O stretching for As(III) and As(V) adsorption by shifting the wavenumber from 1750 cm$^{-1}$ to 1745 cm$^{-1}$ and to 1755 cm$^{-1}$, respectively.[34] FTIR spectrum of GAC/MnFe$_2$O$_4$ composite also showed the intense bands at 1563 cm$^{-1}$ which shifted to 1552 cm$^{-1}$ (As(III)) and to 1542 cm$^{-1}$ (As(V)) that indicated the responsibility of aromatic –NO$_2$ group for the adsorption process. Wavenumber shifted from 1371 to 1382 cm$^{-1}$ (As(III)) and to 1382 cm$^{-1}$ As(V) assigned the reactivity of carboxylate anion C=O stretching for the adsorption process.[35] Wavenumber shifted from 1226 cm$^{-1}$ to 1237 cm$^{-1}$ and to 1247 cm$^{-1}$ assigned for –SO$_3$ stretching for the adsorption of As(III) and As(V), respectively. Wavenumber 1045 cm$^{-1}$ shifted to 1035 cm$^{-1}$ (As(III)) and to 1056 cm$^{-1}$ (As(V)) indicated the Si–O stretching, active for the adsorption process. The band at 585 cm$^{-1}$ could be attributed to the existence of Fe–O bond,[36,37] but then it shifted to 600 cm$^{-1}$ after adsorption of As(III) and to 615 cm$^{-1}$ after adsorption of As(V). A typical peak at 553 cm$^{-1}$ could be assigned to Mn–O bond[38,39] and it had a different variability to 533 and 502 cm$^{-1}$ for adsorption of As(III) and As(V), respectively. The change in wavenumber of Me–O (Me = Fe/Mn) bonds after adsorption of As(III) and As(V) indicated that both Fe–O and Mn–O bonds were responsible for both MnFe$_2$O$_4$–As(III) and MnFe$_2$O$_4$–As(V).[37,40] Presence of As(III) and As(V) on the adsorbent can be assured from the bands appeared at 797 and 828 cm$^{-1}$, respectively.[41–43] It has to be cited here that a clear band was very hard to be obtained in the case of As(III), compared with the distinctive band of As(V) found at 828 cm$^{-1}$. This may be because of different mechanisms involved in As(III) and As(V) adsorption. It should be distinguished that the As–O band after adsorption of arsenic was not clearly observed because of the broad overlapping peaks in this region.[40]

4.1.3. SEM analysis

The SEM images of acid-treated GAC, the prepared unloaded GAC/MnFe$_2$O$_4$ composite and GAC/MnFe$_2$O$_4$ composite loaded with As(III) and GAC/MnFe$_2$O$_4$ composite loaded with As(V) are presented in Figure 4(a)–(d), respectively. Figure 4(a) confirmed that several pores homogeneously pervaded onto the pure acid-treated GAC surface. It can be observed from Figure 4(b), manganese ferrite (MnFe$_2$O$_4$) particles with several diameters were randomly distributed onto the acid-treated GAC surface. Though the surface of acid-treated GAC was shielded by various trivial aggregates of MnFe$_2$O$_4$ after being merged, a slight porous structure could still be seen, which preserved high adsorption capacities of
the acid-treated GAC. A change in surface morphology from being smooth to rough and occupation of pores indicated the As(III) and As(V) adsorption on the surface and pores of GAC/MnFe₂O₄ composite giving it a rough texture. [44]

The corresponding EDX spectra of the unloaded and loaded composite are collected and given in Figure 4(a)–(d). The presence of iron, manganese and oxygen on the unloaded composite surface and iron, manganese and oxygen, arsenic on the loaded composite surface were exposed evidently. This outcome again established the occurrence of MnFe₂O₄ particles onto the acid-treated GAC surface as well as adsorption of arsenic onto the surface of composite.

### 4.2. Effect of pH

Since both the distribution of arsenic ions in natural water and the overall charge of the adsorbent mostly depend on pH conditions,[45,46] so pH plays a significant governing role in the adsorption process to attain maximum arsenic scavenging by an adsorbent.[35] Hence, the effect of pH on adsorption of As(III) and As(V) by GAC/MnFe₂O₄ composite has
been monitored by changing the initial pH of the solution in the range of 2.0–12.0 and the results are shown in Figure 5. The dependency of uptake of adsorbate on pH is associated to both functional groups on the surface of adsorbents and to chemistry of the adsorbate in aqueous phase. The pH value can alter the state of the active-binding sites.

In the pH range of 2.0–9.0 and 10.0–12.0, As(III) occurs mostly in neutral (H₃AsO₃) and anionic (H₂AsO₄⁻) forms, respectively. Reports also confirm that As(V) exists mainly in the monovalent form of H₂AsO₄⁻ in the pH range of 3.0–6.0, nevertheless, at pH near 2.0, a small extent of H₃AsO₄ also remains. Whereas a divalent anion HAsO₂⁻ predominates at higher pH values (>8.0); both species co-exist, in the intermediate region of pH 6.0–8.0.[16]

Change in the % removal in the pH range of 2.0–5.0 was 36.5–57.4% in case of As(III) and subsequently scavenging increased sharply from 57.4 to 88.7% from pH 5.0 to 7.0 and reached a maximum at pH 7.0. After that, a sharp decline in the removal was observed. The adsorbent surfaces are vastly protonated in extreme acidic conditions and such a condition is not so encouraging for the removal of As(III) due to the existence of neutral As(III) species in this range, causing virtually no alteration in the degree of adsorption within the pH range of 2.0–5.0. The degree of protonation of the surface decreases progressively, with the rise in pH of the system. The maximum scavenging of As(III) was at pH 7.0 where merely nonionic species H₃AsO₃ are prevailing, might be attributed to several products of undetermined reaction during the process of adsorption. The neutral species (H₃AsO₃) cannot undergo electrostatic interaction with the adsorbent. However, such species can interact with the unprotonated amino groups.[43,47] The negative charged H₂AsO₄⁻ species begins governing in alkaline medium and thus surface also inclines to gain negative charges (OH⁻). This trend of adsorbate species and adsorbent surface will endure to rise with the rise of pH affecting an ongoing rise in the repulsive forces between the adsorbate species and adsorbent surface causing a reduction in adsorption.[16]
For As(V), initially the removal enhanced from pH 2.0 to 4.0, reached a maximum at pH 4.0 and formerly reduced with further rise in the pH up to 12.0. At pH 2.0–4.0 neutral (H₃AsO₄) and anionic (H₂AsO₄⁻) species occur, though the dominating is H₂AsO₄⁻. At low pH (2.0–4.0), the adsorbent surface is extremely protonated and thus a strong electrostatic interaction remains between positively charged adsorbent surface and oxyanions and as a consequence the removal improved in this pH range due to the rise in H₂AsO₄⁻ species with the pH. The dominant species of As(V) in the above-mentioned pH range are H₂AsO₄⁻ ions, which can be adsorbed on the adsorbent by substituting hydroxyl ions or coordination of hydroxyl groups with the adsorbate.[47] The further reduction in the removal of As(V) with rise in pH (4.0–12.0) may be elucidated as, the adsorbent may be negatively charged by adsorbing hydroxyl ions onto the surface or by ionization of very weak acidic functional groups of the adsorbent, or both at higher pH values. A repulsive force may exist between the anionic species and negatively charged surface. This results in reduced As(V) removal at higher pH values.[16]

Yet, a definite number of As(III) and As(V) ions were still adsorbed on the GAC/MnFe₂O₄ composite at pH > 7.0 and pH > 4.0, respectively (Figure 6) and therefore there must be another mechanisms tangled in this chemical process. Due to the greater affinity of As(III) and As(V) anions with metal oxide than that of hydroxide with metal oxide, the As(III) and As(V) can substitute the hydroxide from the surface of the hydrolyzed metal oxides. It is proposed that ion exchange is also engaged in addition to electrostatic repulsion in this pH range.

Zhang et al. [17] also described the slight effect of pH on the scavenging of As(III) by CoFe₂O₄ and MnFe₂O₄ within pH range of 3.0–10.0 by their study for 24 h contact time. They have also stated that for the further As(III) adsorption study, the solution was set at pH 7.0. They have also stated that the adsorption of As(V) adsorption clearly depended on pH, and the removal was maximum under acidic conditions (pH 3.0). Parsons et al. [18]
reported that the adsorption investigated using 100 μg/L of either As(III) or (V) was pH independent from pH 2.0 through pH 6.0. Another study by Ranjan et al. [16] presented similar pH dependency of As(III) binding to a low-cost rice polish adsorbent with very high binding at pH 7.0 and decreasing binding at higher pH and for As(V) maximum removal was found at pH 4.0 and then decrease with increasing pH. Mondal et al. [41] also reported that removal of arsenic (As(T) i.e. As(III) and As(V)) was less effected with the variation of pH within the pH range of 2.0–11.0. Highest scavenging of As(V) and As(III) was detected in the pH range of 5.0–7.0 and 9.0–11.0, respectively, for both GAC and GAC–Fe.

4.3. Adsorption mechanism of As(III) and As(V) ions with GAC/MnFe₂O₄ composite

The mechanism of any adsorption process is very significant section to understand the characteristics of the material as well as to know the process, which supports in designing an innovative adsorbent for upcoming uses. Surface sites are positively charged at lower pH of the medium and consequently attract negatively charged As(III) and As(V) by an electrostatic interaction or Coulombic force.[48,49]

MnFe₂O₄ is mainly responsible to develop the charge on the surface of adsorbent when GAC/MnFe₂O₄ composite comes in contact with water. The GAC/MnFe₂O₄ composite surface fulfils the coordination shells with the existing OH group with the materials under hydration.[50] With the change in pH, these surface-active OH groups may again bind or release H⁺ where the surface remains positive. As the affinity of AsO₃⁻⁻ or H₂AsO₃⁻ and AsO₄⁻⁻ or H₂AsO₄⁻ anions with metal oxide is higher than that of hydroxide with metal oxide, the AsO₃⁻⁻ or H₂AsO₃⁻ and AsO₄⁻⁻ or H₂AsO₄⁻ can substitute the hydroxide from the surface of the hydrolyzed metal oxides.

Depending on the contact methods and relative concentrations, interactions between metals and hydrous oxides can comprise: (1) adsorption, a surface complexation reaction between metal adsorbates and surface sites, which is restricted to the accumulation of adsorbate onto the external surface of a solid; (2) absorption or diffusion into the solid [51]; (3) surface precipitation, formation of a multilayer solid phase on the oxide surface [52]; and (4) coprecipitation, the simultaneous precipitation of the adsorbate ion with the hydrous oxide phase.[53] These processes can act simultaneously and differentiating them is challenging. The governance of one particular process needs analytical methods with molecular-scale resolution such as chemical measurements and advanced analytical techniques, such as spectroscopy at electron microscopic scales.[51] Though, there is no reason that monolayer surface coverage must be finished before the beginning of multilayer coverage, i.e. surface precipitation. The transition from adsorption to precipitation may occur before the surface sites are saturated. In the cases where precipitation has been detected, the transition from adsorption to precipitation is smooth and there is no obvious interruption in the adsorption isotherms for indicating the start of precipitation.[54]

(1) The surface of adsorbent would obtain a positive charge when pH was <7.0 owing to the following reaction [37,41,50,55,56]:

\[ \equiv \text{MeOH}_{(\text{surf})} + \text{H}_{3}\text{O}^{+}_{(\text{aq})} \rightarrow \equiv \text{MeOH}_{2}^{+} + \text{H}_{2}\text{O} \]  

where Me denoted the surface of MnFe₂O₄.

When pH > 7.0, a negative charge had been developed on the surface of GAC/MnFe₂O₄:
(a) Thus when pH < 7.0, the overall mechanism of As(III) or As(V) adsorption can be characterized in three different forms [50,56]:

(i) electrostatic interaction or coulombic interaction between positively charged centre (nitrogen, OH) and negatively charged As(III) or As(V) in solution,

(ii) electrostatic attraction between positively charged surface, hydroxyl group and $\text{AsO}_3^{3-}$ or $\text{H}_2\text{AsO}_5^{3-}$ and $\text{AsO}_4^{5-}$ or $\text{H}_2\text{AsO}_4^{5-}$ [57]:

$$\equiv \text{MeOH}_{(\text{surf})}^+ + \text{OH}^-_{(aq)} \rightarrow \equiv \text{Me}^+ - \text{O}^- + \text{H}_2\text{O} \quad (7)$$

and (iii) ion exchange reaction between positively charged metal centre and $\text{H}_2\text{AsO}_3^{3-}$ and $\text{H}_2\text{AsO}_3^{3-}$ or $\text{H}_2\text{AsO}_4^{5-}$:

$$\equiv \text{MeOH}_2^+ + \text{H}_2\text{AsO}_3^- \rightarrow \text{MeOH}_2^+ \cdots -\text{O}_3\text{AsH}_2 \text{ (electrostatic attraction) } \quad (8)$$

$$\equiv \text{MeOH}_2^+ + \text{H}_2\text{AsO}_4^- \rightarrow \text{MeOH}_2^+ \cdots -\text{O}_4\text{AsH}_2 \text{ (electrostatic attraction) } \quad (9)$$

(b) Again when the pH of the solution remains moderately in a neutral range, (pH 7.0), biosorption of As(III) or As(V) on the neutral adsorbent surface can be defined by a ligand or ion exchange reaction mechanism, which is characterized as follows [50,56]:

$$\equiv \text{MeOH} + \text{AsO}_3^{3-} \rightarrow \text{Me}^+ \cdots \text{AsO}_3^{3-} + \text{OH}^- \text{ (ligand or ion exchange) } \quad (12)$$

$$\equiv \text{MeOH} + \text{H}_2\text{AsO}_3^{3-} \rightarrow \text{Me}^-\text{OAsO}_3\text{H}_2 + \text{2H}_2\text{O} \text{ (ion exchange) } \quad (13)$$

$$\equiv \text{MH} + \text{AsO}_4^{5-} \rightarrow \text{M}^+ \cdots \text{AsO}_4^{5-} + \text{OH}^- \text{ (ligand or ion exchange) } \quad (14)$$

$$\equiv \text{MeOH} + \text{H}_2\text{AsO}_4^- \rightarrow \text{Me}^-\text{OAsO}_4\text{H}_2 + \text{OH}^- \text{ (ligand or ion exchange) } \quad (15)$$

(c) At pH above > 7.0, the surface is hydroxylated and expressed as MeO$^-$ and the negatively charged surface can exchange AsO$_3^{3-}$ or H$_2$AsO$_3^-$ and AsO$_4^{5-}$ or H$_2$AsO$_4^-$ anions as follows [57]:

$$\equiv \text{MeO}^- + \text{AsO}_3^{3-} + \text{H}_2\text{O} \rightarrow \text{MeOH}^-\text{AsO}_3^{3-} + \text{OH}^- \quad (16)$$

$$\equiv \text{MeO}^- + \text{H}_2\text{AsO}_3^- + \text{H}_2\text{O} \rightarrow \text{MeOH}^-\text{AsO}_3^{3-} + \text{OH}^- \quad (17)$$

$$\equiv \text{MeO}^- + \text{AsO}_4^{5-} + \text{H}_2\text{O} \rightarrow \text{MeOH}^-\text{AsO}_4^{5-} + \text{OH}^- \quad (18)$$

$$\equiv \text{MeO}^- + \text{H}_2\text{AsO}_4^- + \text{H}_2\text{O} \rightarrow \text{MeOH}^-\text{AsO}_4^{5-} + \text{OH}^- \quad (19)$$

Formation of MnFe$_2$O$_4$ layer enhanced the net positive charge of the GAC/MnFe$_2$O$_4$ and improved the arsenic adsorption capacity. The iron and manganese in GAC/MnFe$_2$O$_4$ composite triggered the oxidation of As(III) to As(V), which can easily be adsorbed by the adsorbent in the experimental pH range. [58] In case of GAC, As(III) did not oxidize to As(V). So the binding of the As(III) or As(V) to the surface of the GAC/MnFe$_2$O$_4$ adsorbent generally
resulted in higher binding capacities owing to the probable various electron transfers from either the Mn or Fe ions.[18]

So the removal of $\text{AsO}_3^{3-}$ or $\text{H}_2\text{AsO}_3^-$ and $\text{AsO}_4^{3-}$ or $\text{H}_2\text{AsO}_4^-$ on GAC/MnFe$_2$O$_4$ composite was supposed to involve adsorption, precipitation, coprecipitation and solid diffusion depending on a number of peripheral parameters such as the solid surface site, temperature, initial concentration, pH and time in addition to the density of surface functional groups existing for coordination. One probable complicating factor is the beginning of surface precipitation during the 'adsorption' reaction.[54] A similar result was found for the removal of phosphate using goethite ($\alpha$-FeOOH) by Li and Stanforth [54]. Li and Stanforth [54] reported that the reaction between phosphate and goethite changes from adsorption onto surface precipitation did not alter the adsorption isotherm.[55] So among all the processes, adsorption and surface precipitation mechanism were mainly responsible for the removal of As(III) and As(V). Surface precipitation can be observed as a solid solution, or as a tertiary adsorption process, in which the metal ion is biosorbed on the sorbed arsenic (either As(III) or As(V)) to form the surface precipitate.[54]

The surface precipitation model has been utilized mainly for cations, where the cation was precipitating as a hydroxide on the oxide/hydroxide surface.[52,59–62] It has been utilized sparingly to describe anion adsorption/precipitation. Dzombak and Morel [63] suggested that only a fixed amount of surface precipitation would happen for anions, as the source of cations was limited.

Li and Stanforth [54] reported anion precipitation occurred at the expense of the adsorbent including high anion concentrations throughout experiments. In the present study, anion precipitation also happened at the expense of the adsorbent (GAC/MnFe$_2$O$_4$ composite) including high concentration of arsenic (either As(III) or As(V)). The surface precipitation model usually contains an initial, fast adsorption mechanism followed by a slower surface precipitation. So there is adsorption onto the surface with a surface precipitation layer covering the adsorbed layer.[64] SEM results did not expose the formation of new phases due to precipitation or coprecipitation after the sorption reactions.[54] A rough sketch of the conceptual model is presented in Figure 6 on the basis of figures from Banwart [65] and Dzombak and Morel [63].

### 4.4. Effect of adsorbent dose

Adsorbent dose is also a significant factor which governs the uptake of adsorbent for an initial adsorbate concentration. The influence of adsorbent dose on the % removal is shown in Figure 7. The removal of As(III) and As(V) enhanced up to 88.7 and 91.2%, respectively, when the dose of adsorbent was increased from 0.1 to 1 g/L, while further rise in adsorbent dose up to 10 g/L had no impact on the scavenging of arsenic. The increase in adsorbent dose (0.1–1 g/L) resulted in a fast increase in arsenic ions adsorption. This result can be clarified by the statements that during the adsorption process, larger surface area was available and the adsorption sites remain unsaturated while the number of sites available for the adsorption increases with an increase in the adsorbent dose. With the rise in adsorbent dose the number of active sites in unit volume of solution increases, which leads to the increase in the % removal of arsenic.[41] However with further increase in adsorbent dose (2–10 g/L), there was no noteworthy variation in the % removal of As(III) and As(V) ions. It may also be owing to the fact that a higher dosage could generate a ‘screen effect’ on the surface of
adsorbent, protecting the binding sites, thus the lower arsenic adsorption.[50] The reduction in removal efficiency at higher adsorbent dose can also be explained as a result of a partial aggregation of adsorbents, which consequences in a reduction in effective surface area for the adsorption and overlapping of active sites.[66,67] Hence for further studies, 1 g/L of GAC/MnFe₂O₄ composite was chosen as the optimum adsorbent dose.

The optimum adsorbent dose for nanoscale zero-valent iron has been found to be 1 g/L to remove As(III) from 1 mg/L solution.[68] The highest scavenging efficiency of As(III) 89% was found using 1 g/L of iron impregnated activated carbon, whereas for As(V) was 68% at pH 7.5.[69]

4.5. Effect of contact time

Figure 8 represents the influence of contact time on the % removal of As(III) and As(V). The time mandatory to achieve equilibrium for both As(III) and As(V) adsorption onto GAC/MnFe₂O₄ composite was 70 min. Further increase in time, no noteworthy improvements were found in scavenging arsenic. Hence further adsorption experiments were continued for a contact time of 70 min.

From the results it is further prominent that in all the systems, the saturation time does not depend on the adsorbate concentration in the solution. The change in the rate of removal might be because of the fact that firstly all adsorbent sites are easily available and also the concentration gradient of adsorbate is very high. At optimum pH, the fast kinetics of interaction of adsorbent–adsorbate might be agreed to improve availability of the active sites of the adsorbent. Therefore, the removal of adsorbate was fast in the early stages and progressively reduces with the interval of time until equilibrium in each case. The decrease in removal of metal ion at the later stage of the process was owing to the reduction in concentration
of metal ions.[70] Thus the curves found were single, smooth and continuous leading to equilibrium and recommended the possibility of monolayer coverage of the adsorbate on the adsorbent surface.[16]

The maximum removal of As(V) ions has been attained in 80 and 60 min onto Salvadora persica stem ash obtained at 300 °C and Salvadora persica stem ash obtained at 500 °C, respectively.[71] Highest As(III) removal of 82.2% has been found at contact time of 90 min using banana peel (condition: optimized pH 7.0, dose of 8 g/L, temperature of 35 °C and 10 mg/L As(III) ion concentration) by Kamsonlian et al. [72].

4.6. Effect of temperature

The temperature has two main effects on the adsorption process. Increasing the temperature is acknowledged to raise the rate of diffusion of the adsorbate, due to the reduction in the viscosity of the solution. Moreover, varying the temperature will alter the equilibrium adsorption capacity of the adsorbent for a specific adsorbate.[73]

The influence of temperature on the scavenging efficiency of As(III) and As(V) was examined in the range of 20–50 °C during the equilibrium time. The result indicated that the maximum removal was reached at a temperature of 30 °C (Figure 9). Further increase in temperature resulted in lower removal efficiency for arsenic removal by GAC/MnFe₂O₄ composite. This can be elucidated by the spontaneity and exothermicity of the adsorption process. This reduction in removal efficiency might be because of many factors: the relative rise in the dodging tendency of the arsenic ions from the solid adsorbent phase to the bulk liquid phase; deactivating the surface of adsorbent or destroying some active sites onto the surface of adsorbent because of bond ruptures [74,75] or owing to the weakening of adsorptive forces between the adsorbate species and the active sites of the adsorbents and also between the adjacent molecules of adsorbed phase for high temperatures or movement.
of adsorbents with more speed, so, lower interaction time with the adsorbent active sites was obtainable for them.[76,77] Highest removals of As(III) and As(V) were observed at 30 °C by Mondal et al. [78] on GAC–Cu as well as by Mondal et al. [41] on GAC and GAC–Fe. Similar trend was reported by Roy et al. [77] using iron impregnated sugarcane carbon and Saqib et al. [79] using Blue Pine (Pinus wallichiana) and Walnut (Juglans regia).

4.7. Effect of initial arsenic concentration

Effect of initial metal ion concentration on the % removal of arsenic is shown in Figure 10. With rise in initial arsenic concentrations, more arsenic ions are left un-adsorbed in the solution owing to the saturation of the binding sites. This specifies that energetically less favourable binding sites become engaged with rising ions concentration in aqueous solution. Adsorption of arsenic ions is accredited to various ion exchange mechanisms along with the adsorption process. Throughout the ion exchange process, the arsenic ions have to be transferred through the adsorbent pores, but also through the lattice channel, they have to be replaced exchangeable anions. Diffusion was faster through pores and was arrested when the ion transfers through the channels with smaller diameter. Here, the adsorption of arsenic ion is mostly credited to ion exchange reactions in the adsorbents micro pores.[80]

4.8. Model selection: error analysis and maximum adsorption capacity

The optimum parameter sets, estimated based on higher correlation coefficients ($R$, $R^2$, $\bar{R}^2$) and lower error values (SSE, Reduced $\chi^2$ and Root-MSE), were evaluated by considering 95% confidence interval. The ideal parameters along with the correlation coefficients and error values are given in the Tables 57.
4.8.1. One-parameter model

Henry’s law was smeread for defining the experimental data obtained for the adsorption of arsenic (As(III) and As(V)) onto GAC/MnFe₂O₄ composite (Figure 11(a) and (b)). The poor error values (SSE, Reduced $\chi^2$ and Root-MSE) and lower correlation coefficients ($R$, $R^2$ and $\bar{R}^2$) for both As(III) and As(V) indicated that this model is extremely unsuccessful to predict the equilibrium data (Table 5). It might be because of the nonavailability of adsorption data in the vanishing range of arsenic. Generally, in liquid phase adsorption, the equilibrium adsorption data are attained at higher equilibrium adsorbate concentrations, where the adsorbent surface is virtually at the edge of saturation. So, this research demonstrated the fact of letdown of Henry’s law at the high ranges of residual adsorbate concentration.

4.8.2. Two-parameter model

Among all the other two-parameter models (Figure 11(a) and (b)) and Table 5, the Langmuir isotherm exhibited a good fit to the experimental data for both As(III) and As(V) owing to the highest correlation coefficients ($R$, $R^2$ and $\bar{R}^2$) and the lowest error values (SSE, Reduced $\chi^2$ and Root-MSE) (Table 5) and a high $q_{ml}$ value. This verified the homogeneous and monolayer manner of adsorption of As(III) and As(V) onto GAC/MnFe₂O₄ composite. Furthermore, it gave support to the assumption that adsorption of As(III) and As(V) happened uniformly on the active sites of the adsorbent and once a molecule occupies a site, no more adsorption could happen at this site. The separation factor ($R_L$) value (Figure 12) which is a measure of adsorption favourability estimated from the Langmuir isotherm specified that As(III) and As(V) adsorption onto GAC/MnFe₂O₄ composite was in favourable region ($0 < R_L < 1$). The reduction in $R_L$ with an increase in the initial concentration specifies that the adsorption was more favourable at high concentrations.

Alternatively, the obtained correlation coefficients ($R$, $R^2$ and $\bar{R}^2$) and low error values (SSE, Reduced $\chi^2$ and Root-MSE) in case of the Jovanovic model confirmed better fit with
In order, the Freundlich isotherm (Table 5) virtually fitted to the equilibrium data in support of the assumptions of heterogeneous manner of adsorption to a certain extent owing to high correlation coefficients and low error values. But the Freundlich isotherm model did not fit as well as Langmuir and Jovanovic isotherms. The respective value of $n_F$ of the Freundlich isotherm exhibited that the adsorption of both As(III) and As(V) onto GAC/MnFe$_2$O$_4$ composite was favourable adsorption.

The obtained high correlation coefficients and low error values of activated sludge isotherm model confirmed the better fit of equilibrium data as compared with the Temkin,
Table 5. Isotherm constants of one-parameter and two-parameter models for As(III) and As(V) adsorption on GAC/MnFe$_2$O$_4$ composite.

| Isotherm models       | Parameters          | Values for As(III) | Values for As(V) |
|-----------------------|---------------------|--------------------|------------------|
| Henry                 | $K_{H}$ (L/g)       | 1.13               | 1.38             |
|                       | Reduced $\chi^2$    | 25,900             | 33,200           |
|                       | $\text{SSE}$        | 259,000            | 332,000          |
|                       | $R$                 | 0.896              | 0.889            |
|                       | $R^2$               | 0.803              | 0.791            |
|                       | $\overline{R}^2$   | 0.803              | 0.791            |
|                       | Root-MSE            | 161                | 182              |
| Langmuir              | $q_{\text{ml}}$ (mg/g) | 1253              | 1314             |
|                       | $K_L$ (L/mg)        | 0.003              | 0.004            |
|                       | Reduced $\chi^2$    | 484                | 1300             |
|                       | $\text{SSE}$        | 4400               | 11,000           |
|                       | $R$                 | 0.998              | 0.997            |
|                       | $R^2$               | 0.997              | 0.993            |
|                       | $\overline{R}^2$   | 0.996              | 0.992            |
|                       | Root-MSE            | 22.0               | 34.8             |
| Freundlich            | $K_F ((\text{mg/g})(\text{L/mg})^{1/n_f})$ | 32.1               | 41.8             |
|                       | $n_f$               | 2.02               | 2.09             |
|                       | Reduced $\chi^2$    | 1400               | 1500             |
|                       | $\text{SSE}$        | 12,700             | 13,500           |
|                       | $R$                 | 0.995              | 0.996            |
|                       | $R^2$               | 0.990              | 0.992            |
|                       | $\overline{R}^2$   | 0.989              | 0.991            |
|                       | Root-MSE            | 37.5               | 38.6             |
| Temkin                | $b_{TE}$ (J/mol)    | 13.6               | 12.8             |
|                       | $K_{TE}$ (L/mg)     | 0.104              | 0.132            |
|                       | Reduced $\chi^2$    | 8400               | 9000             |
|                       | $\text{SSE}$        | 75,500             | 80,400           |
|                       | $R$                 | 0.971              | 0.974            |
|                       | $R^2$               | 0.943              | 0.949            |
|                       | $\overline{R}^2$   | 0.936              | 0.944            |
|                       | Root-MSE            | 91.6               | 94.5             |
| Dubinin–Radushkevich | $q_{\text{mDR}}$ (mg/g) | 870                | 923              |
|                       | $K_{DR}$ (mol$^2$/KJ$^2$) | 0.004              | 0.002            |
|                       | $E$ (kJ/mol)        | 11.9               | 15.8             |
|                       | Reduced $\chi^2$    | 8700               | 13,500           |
|                       | $\text{SSE}$        | 77,900             | 122,000          |
|                       | $R$                 | 0.970              | 0.961            |
|                       | $R^2$               | 0.941              | 0.924            |
|                       | $\overline{R}^2$   | 0.934              | 0.915            |
|                       | Root-MSE            | 93.0               | 116              |
| Activated sludge      | $K_{m}$ (L/g)       | 14.5               | 19.4             |
|                       | $N_n$               | 2.02               | 2.09             |
|                       | Reduced $\chi^2$    | 1400               | 1500             |
|                       | $\text{SSE}$        | 12,700             | 13,500           |
|                       | $R$                 | 0.995              | 0.996            |
|                       | $R^2$               | 0.990              | 0.992            |
|                       | $\overline{R}^2$   | 0.989              | 0.991            |
|                       | Root-MSE            | 37.5               | 38.6             |
| Jovanovic             | $q_{\text{mJV}}$ (mg/g) | 965                | 1038             |
|                       | $K_{m}$ (L/g)       | 0.003              | 0.004            |
|                       | Reduced $\chi^2$    | 1100               | 2700             |
|                       | $\text{SSE}$        | 9901               | 23,800           |
|                       | $R$                 | 0.996              | 0.992            |
|                       | $R^2$               | 0.992              | 0.985            |
|                       | $\overline{R}^2$   | 0.992              | 0.983            |
|                       | Root-MSE            | 33.2               | 51.4             |
Dubinin–Radushkevich isotherm model. But the activated sludge isotherm model was not as good as Langmuir and Jovanovic isotherms. A low level of $K_m$ for both As(III) and As(V) acquired from activated sludge isotherm recommended that the tendency of the formation of floc was probable but little. A lower value of $1/N_m (<1)$ obtained from the activated sludge isotherm proposed that any huge alteration in the equilibrium arsenic concentration would not result in a notable alteration in the amount of floc of arsenic formed using the GAC/MnFe$_2$O$_4$ composite.

Temkin and Dubinin–Radushkevich model did not fit well with the experimental data owing to low correlation coefficients and high error values than those for the Langmuir isotherm model (Table 5) referred that the mechanism of adsorption did not proceed either with progressive widening of adsorbent surfaces or heterogeneous adsorption mode in total (Figure 11(a) and (b)). The mean free energy of adsorption, $E$ for As(III) and As(V) obtained from Dubinin–Radushkevich has been indicating that the adsorption of both As(III) and As(V) using GAC/MnFe$_2$O$_4$ composite occurred by ion exchange adsorption. The larger value of $b_{TE}$ for both As(III) and As(V) acquired from the Temkin isotherm indicated that the interaction between As(III) or As(V) and GAC/MnFe$_2$O$_4$ composite was strong and the positive value of $b_{TE}$ specified an exothermic process. Hence, the adsorption process of As(III) and As(V) on GAC/MnFe$_2$O$_4$ composite can be expressed as chemisorption mechanism, as indicated by the value of $b_{TE}$.

4.8.3. Three-parameter model

The capabilities of the three-parameter equations for modelling the equilibrium adsorption data were tested using nonlinear regression analysis and their isotherm parameters are shown in Figure 13(a), (b) and Table 6. All the models suitably simulated the adsorption isotherms of the studied systems and the equilibrium As(III) and As(V) uptake by GAC/MnFe$_2$O$_4$ composite was soundly well represented with are good correlation coefficients ($R$, $R^2$ and $\overline{R^2}$) and low error values (SSE, Reduced $\chi^2$ and Root-MSE). The suitability of
Table 6. Isotherm constants of three-parameter models for As(III) and As(V) adsorption on GAC/Mn-Fe₂O₄ composite.

| Isotherm models       | Parameters                  | Values for As(III) | Values for As(V) |
|-----------------------|-----------------------------|--------------------|------------------|
| **Redlich–Peterson**  | $K_{rp}$ (L/g)              | 5.30               | 9.70             |
|                       | $q_{rp}$ (L/mg)$^\beta$    | 0.019              | 0.054            |
|                       | $\beta_{rp}$               | 0.796              | 0.722            |
|                       | Reduced $\chi^2$            | 293                | 368              |
|                       | SSE                         | 2400               | 3000             |
|                       | $R$                         | 0.999              | 0.999            |
|                       | $R^2$                       | 0.998              | 0.998            |
|                       | Root-MSE                    | 17.1               | 19.2             |
| **Sips**              | $q_{ms}$ (mg/g)             | 1543               | 1873             |
|                       | $K_s$ ((m/Lg)$^{-1/m_s}$)   | 0.006              | 0.009            |
|                       | $m_s$                       | 0.816              | 0.728            |
|                       | Reduced $\chi^2$            | 284                | 509              |
|                       | SSE                         | 2300               | 4100             |
|                       | $R$                         | 0.999              | 0.999            |
|                       | $R^2$                       | 0.998              | 0.997            |
|                       | Root-MSE                    | 16.8               | 22.6             |
| **Toth**              | $K_t$ (L/mg)                | 0.003              | 0.005            |
|                       | $q_{mt}$ (mg/g)             | 1583               | 2834             |
|                       | $m_t$                       | 0.708              | 0.423            |
|                       | Reduced $\chi^2$            | 323                | 428              |
|                       | SSE                         | 2600               | 3500             |
|                       | $R$                         | 0.999              | 0.999            |
|                       | $R^2$                       | 0.998              | 0.997            |
|                       | Root-MSE                    | 18.0               | 20.7             |
| **Brouers–Sotolongo** | $q_{ms}$ (mg/g)             | 1161               | 1391             |
|                       | $K_{bs}$ ((mg/g)(L/mg)$^{1/a}$) | 0.009   | 0.014            |
|                       | $a$                         | 0.752              | 0.673            |
|                       | Reduced $\chi^2$            | 321                | 593              |
|                       | SSE                         | 2600               | 4800             |
|                       | $R$                         | 0.999              | 0.999            |
|                       | $R^2$                       | 0.998              | 0.997            |
|                       | Root-MSE                    | 17.9               | 24.3             |
| **Vieth–Sladek**      | $K_{vs}$ (L/mg)             | 0.258              | 0.442            |
|                       | $q_{mv}$ (mg/g)             | 832                | 732              |
|                       | $\beta_{vs}$               | 0.005              | 0.009            |
|                       | Reduced $\chi^2$            | 281                | 248              |
|                       | SSE                         | 2300               | 2000             |
|                       | $R$                         | 0.999              | 0.999            |
|                       | $R^2$                       | 0.998              | 0.999            |
|                       | Root-MSE                    | 16.8               | 15.7             |
| **Koble–Corrigan**    | $A_{KC}$ ((mg/g)(L/mg)$^{1/n_{KC}}$) | 3.68            | 4.93             |
|                       | $B_{KC}$ (L/g)$^{n_{KC}}$   | 0.003              | 0.004            |
|                       | $n_{KC}$                    | 1.000              | 1.002            |
|                       | Reduced $\chi^2$            | 544                | 1222             |
|                       | SSE                         | 4400               | 11,000           |
|                       | $R$                         | 0.998              | 0.997            |
|                       | $R^2$                       | 0.997              | 0.993            |
|                       | Root-MSE                    | 23.3               | 35.0             |

(Continued).
Table 6. (Continued).

| Isotherm models          | Parameters                  | Values for As(III) | Values for As(V) |
|--------------------------|-----------------------------|--------------------|------------------|
| Khan                     | $q_{mx}$ (mg/g)             | 576                | 403              |
|                          | $b_x$ (L/mg)                | 0.008              | 0.020            |
|                          | $a_x$                       | 0.722              | 0.657            |
|                          | Reduced $\chi^2$            | 299                | 335              |
|                          | SSE                         | 2400               | 2700             |
|                          | $R$                         | 0.999              | 0.999            |
|                          | $R^2$                       | 0.998              | 0.998            |
|                          | Root-MSE                    | 17.3               | 18.3             |
| Hill                     | $n_a$                       | 0.816              | 0.728            |
|                          | $K_n$ (L/g)                 | 177                | 113              |
|                          | $q_{mx}$ (mg/g)             | 1542               | 1872             |
|                          | Reduced $\chi^2$            | 284                | 509              |
|                          | SSE                         | 2300               | 4100             |
|                          | $R$                         | 0.999              | 0.999            |
|                          | $R^2$                       | 0.998              | 0.997            |
|                          | Root-MSE                    | 16.8               | 22.6             |
| Jossens                  | $K_J$ ((mg/g)(L/mg))        | 5.30               | 9.70             |
|                          | $J$ (L/mg)$^{1/2}$          | 0.019              | 0.054            |
|                          | $b_J$                       | 0.796              | 0.722            |
|                          | Reduced $\chi^2$            | 293                | 368              |
|                          | SSE                         | 2400               | 3000             |
|                          | $R$                         | 0.999              | 0.999            |
|                          | $R^2$                       | 0.998              | 0.998            |
|                          | Root-MSE                    | 17.1               | 19.2             |
| Fritz-Schlunder-III      | $K_{fs}$ (L/mg)$^{mfs}$     | 0.019              | 0.054            |
|                          | $q_{mx}$ (mg/g)             | 282                | 179              |
|                          | $m_{fs}$                    | 0.796              | 0.722            |
|                          | Reduced $\chi^2$            | 293                | 368              |
|                          | SSE                         | 2400               | 3000             |
|                          | $R$                         | 0.999              | 0.999            |
|                          | $R^2$                       | 0.998              | 0.998            |
|                          | Root-MSE                    | 17.1               | 19.2             |
| Unilan                   | $q_{mu}$ (mg/g)             | 1331               | 1385             |
|                          | $s$                         | 1.00               | 1.00             |
|                          | $K_u$ (L/mg)                | 0.003              | 0.003            |
|                          | Reduced $\chi^2$            | 432                | 1057             |
|                          | SSE                         | 3500               | 8500             |
|                          | $R$                         | 0.999              | 0.997            |
|                          | $R^2$                       | 0.997              | 0.995            |
|                          | Root-MSE                    | 20.8               | 32.5             |
| Holl–Krich               | $q_{mx}$ (mg/g)             | 1543               | 1873             |
|                          | $K_{mx}$ (L/mg)$^{nmix}$    | 0.006              | 0.009            |
|                          | $n_{mx}$                    | 0.816              | 0.728            |
|                          | Reduced $\chi^2$            | 284                | 509              |
|                          | SSE                         | 2300               | 4100             |
|                          | $R$                         | 0.999              | 0.999            |
|                          | $R^2$                       | 0.998              | 1.0              |
|                          | Root-MSE                    | 16.8               | 22.6             |

(Continued).
| Isotherm models          | Parameters | Values for As(III) | Values for As(V) |
|-------------------------|------------|-------------------|-----------------|
| Langmuir–Freundlich     | $q_{mL}$ (mg/g) | 1543              | 1875            |
|                         | $K_{L}$ (L/mg)  | 0.002             | 0.002           |
|                         | $m$          | 0.816             | 0.727           |
|                         | Reduced $\chi^2$ | 284               | 509             |
|                         | SSE          | 2300              | 4100            |
|                         | $R$          | 0.999             | 0.999           |
|                         | $R^2$        | 0.998             | 0.997           |
|                         | $\bar{R}^2$  | 0.998             | 0.997           |
|                         | Root-MSE     | 16.8              | 22.6            |
| Langmuir–Jovanovic      | $q_{mLJ}$ (mg/g) | 1181              | 1447            |
|                         | $K_{LJ}$ (L/mg) | 0.010             | 0.015           |
|                         | $n$          | 0.736             | 0.650           |
|                         | Reduced $\chi^2$ | 325               | 548             |
|                         | SSE          | 2600              | 4400            |
|                         | $R$          | 0.999             | 0.999           |
|                         | $R^2$        | 0.998             | 0.997           |
|                         | $\bar{R}^2$  | 0.998             | 0.997           |
|                         | Root-MSE     | 18.0              | 23.4            |
| Jovanovic–Freundlich    | $q_{mJ}$ (mg/g) | 1161              | 1392            |
|                         | $K_{J}$ (L/mg)  | 0.002             | 0.002           |
|                         | $n$          | 0.751             | 0.673           |
|                         | Reduced $\chi^2$ | 321               | 593             |
|                         | SSE          | 2600              | 4800            |
|                         | $R$          | 0.999             | 0.999           |
|                         | $R^2$        | 0.998             | 0.997           |
|                         | $\bar{R}^2$  | 0.998             | 0.996           |
|                         | Root-MSE     | 17.9              | 24.3            |
| Radke–Prausnitz I      | $K_{RPI}$ (L/mg) | 0.008             | 0.020           |
|                         | $q_{mRPI}$ (mg/g) | 576               | 403             |
|                         | $m_{RPI}$    | 0.722             | 0.657           |
|                         | Reduced $\chi^2$ | 299               | 335             |
|                         | SSE          | 2400              | 3000            |
|                         | $R$          | 0.999             | 0.999           |
|                         | $R^2$        | 0.998             | 0.998           |
|                         | $\bar{R}^2$  | 0.998             | 0.998           |
|                         | Root-MSE     | 17.3              | 18.3            |
| Radke–Prausnitz II     | $q_{mRPII}$ (mg/g) | 282               | 9.71            |
|                         | $K_{RPII}$ (L/mg) | 0.019             | 18.4            |
|                         | $m_{RPII}$   | 0.796             | 0.279           |
|                         | Reduced $\chi^2$ | 293               | 368             |
|                         | SSE          | 2400              | 3000            |
|                         | $R$          | 0.999             | 0.999           |
|                         | $R^2$        | 0.998             | 0.998           |
|                         | $\bar{R}^2$  | 0.998             | 0.998           |
|                         | Root-MSE     | 17.1              | 19.2            |
| Radke–Prausnitz III    | $q_{mRPIII}$ (mg/g) | 5.30              | 9.71            |
|                         | $K_{RPIII}$ (L/mg) | 53.37             | 18.379          |
|                         | $m_{RPIII}$  | 0.204             | 0.279           |
|                         | Reduced $\chi^2$ | 293               | 368             |
|                         | SSE          | 2400              | 3000            |
|                         | $R$          | 0.999             | 0.999           |
|                         | $R^2$        | 0.998             | 0.998           |
|                         | $\bar{R}^2$  | 0.998             | 0.998           |
|                         | Root-MSE     | 17.1              | 19.2            |
these isotherms again proved the homogeneous adsorption on the heterogeneous surface of GAC/MnFe₂O₄ composite and the cooperative manifestations of the adsorptive As(III) and As(V) ions.

### Table 6. (Continued).

| Isotherm models                  | Parameters | Values for As(III) | Values for As(V) |
|----------------------------------|------------|--------------------|------------------|
| Langmuir–Freundlich–Jovanovic    | qₘLfJ (mg/g) | 1200               | 1501             |
|                                  | nₖLfJ      | 0.719              | 0.623            |
|                                  | KₖLfJ (L/mg) | 0.002              | 0.002            |
|                                  | Reduced χ²  | 322                | 524              |
|                                  | SSE        | 2600               | 4200             |
|                                  | R          | 0.999              | 0.999            |
|                                  | R²         | 0.998              | 0.997            |
|                                  | ̄R²        | 0.998              | 0.997            |
|                                  | Root-MSE   | 17.9               | 22.9             |

### Figure 13.
Isotherm modelling of (a) As(III) and (b) As(V) adsorption onto the GAC/MnFe₂O₄ composite for three-parameter models (Cₒ: 50–2000 mg/L; M: 1 g/L; pH: 7.0 (As(III)) and 4.0 (As(V)); t: 70 min; T: 30°C) (error bars represent means ± standard errors from the mean of duplicate experiments).
On the basis of the maximum correlation coefficients \((R, R^2 \text{ and } \bar{R}^2)\) and the lowest error values (SSE, Reduced \(\chi^2\) and Root-MSE) for both As(III) and As(V), the better and faultless representation of the experimental results was achieved using the Vieth–Sladek isotherm among the tested three parameter isotherm. The values of the Vieth–Sladek model exponent \(\beta_{VS}\) for both As(III) and As(V) tending to zero indicated that the data can desirably fit with the Langmuir model. This is ascertained by the suitable fit of the data to the Langmuir model. The Vieth–Sladek isotherm is utilized for calculating diffusion rates in solid materials from transient adsorption. Especially, this isotherm applies to adsorbates which are adsorbed according to a specific isotherm: one defined by a linear component (Henry’s law) and a commonly found nonlinear component (Langmuir equation). The linear component relates physically to gas dissolved in the amorphous regions and the nonlinear to the adherence of gas molecules to sites on the surface of porous adsorbents.\cite{81}

The maximum adsorption capacity predicted by the Sips, Toth, Hill, Unilan, Holl–Krich and Langmuir–Freundlich isotherms were higher than the Langmuir isotherm but it was observed opposite in the case of Brouers–Sotolongo, Vieth–Sladek, Khan, Fritz–Schlunder–III, Langmuir–Jovanovic, Jovanovic–Freundlich, Radke–Prausnitz I, II and III and Langmuir–Freundlich–Jovanovic isotherms for both As(III) and As(V).

The values of \(\beta_{RP}, m_S, m_T, aK, m_{FS}, m_{LP}, n_{LP}, m_{RPI}, m_{RPII}\) and \(n_{LF}\) for both As(III) and As(V) approaching unity indicated that the adsorption data found in this study were more of a Langmuir form rather than that of the Freundlich isotherm. The Radke–Prausnitz model exponent \(m_{RPIII}\) for both As(III) and As(V)) was observed to be close to zero which specified that the model supported Langmuir model.

The Hill model exponent \(n_H\) for both As(III) and As(V) was <1, conveyed the fact that the binding interaction between As(III) or As(V) and GAC/MnFe₂O₄ composite was in the form of negative cooperativity.

Though the correlation coefficient values were moderately good for all the three-parameter models (Table 6), poor error values (SSE, Reduced \(\chi^2\) and Root-MSE) clearly indicated that the Koble–Corrigan and Unilan isotherm failed to fit the experimental equilibrium data may be owing to the fact that the most of the active sites might have adsorption energy higher than maximum value.

### 4.8.4. Four-parameter model

Among the three isotherms of four-parameter models (Figure 14(a) and (b); Table 7), very well fitting of the experimental results of adsorption data for both As(III) and As(V) were found using the Marczewski–Jaroniec isotherm with the highest correlation coefficients \((R, R^2 \text{ and } \bar{R}^2)\) and the lowest error values (SSE, Reduced \(\chi^2\) and Root-MSE). This isotherm was found to be slightly better than Fritz–Schlunder-IV and Baudu, based on correlation coefficients \((R, R^2 \text{ and } \bar{R}^2)\) and error values (SSE, Reduced \(\chi^2\) and Root-MSE).

Moreover, the values of \(n_{MJ}\) and \(m_{MJ}\) approaching unity specified that the adsorption data can preferably be fitted with the Langmuir isotherm in case of As(III). Wherever in case of As(V), the values of \(n_{MJ}\) approaching unity and the values \(m_{MJ}\) are equal to 1 specified that the adsorption data can preferably be fitted with the Toth isotherm. Similarity was also observed between the \(K_{MJ}\) and the Langmuir constant \(K_L\).

High correlation coefficients \((R, R^2 \text{ and } \bar{R}^2)\) and low error values (SSE, Reduced \(\chi^2\) and Root-MSE) clearly indicated that the Fritz–Schlunder-IV isotherm can also be able to fit the experimental equilibrium data. Moreover, the values of \(a_{FS}\) and \(b_{FS}\) for both As(III)
and for As(V)) approaching unity specified that the adsorption data can desirably be fitted with the Langmuir isotherm. The parameters calculated \( A_{FS} \) and \( B_{FS} \) and a value of \( A_{FS}/B_{FS} \) was indicative of the adsorbate adsorbent interaction strength. Similarity was also noted between the \( B_{FS} \) and the Langmuir constant \( K_L \).

Fritz–Schlunder-IV and Baudu isotherms yet again confirmed the idea that the adsorption of As(III) and As(V) onto GAC/MnFe₂O₄ composite was homogeneous and characteristically followed the Langmuir isotherm nevertheless the adsorption was proceeding on the heterogeneous surface.

![Figure 14](image)

Figure 14. Isotherm modelling of (a) As(III) and (b) As(V) adsorption onto the GAC/MnFe₂O₄ composite for four and five-parameter models (\( C_0: 50–2000 \) mg/L; \( M: 1 \) g/L; pH: 7.0 (As(III)) and 4.0 (As(V)); \( t: 70 \) min; \( T: 30 \) °C) (error bars represent means ± standard errors from the mean of duplicate experiments).
The adsorption data were analysed in keeping with the nonlinear form of the five-parameter isotherm model of Fritz–Schlunder-V. A satisfactory fitting of the experimental data of the adsorption isotherms attained using the five-parameter model of Fritz–Schlunder-V (Figure 14(a) and (b); Table 7) with the highest correlation coefficients ($R$, $R^2$ and $\overline{R}^2$) and the lowest error values (SSE, Reduced $\chi^2$ and Root-MSE) was found. The values of $\alpha_{FS}$ and $\beta_{FS}$ for both As(III) and As(V) were very near to unity which exhibited that the adsorption data followed the assumptions of the Langmuir isotherm.
4.9. Final remarks on isotherm study

The experimental equilibrium data are observed to be well fitted with Langmuir isotherm model among two-parameter isotherm models which indicated the monomolecular adsorption of As(III) and As(V) onto GAC/MnFe$_2$O$_4$ composite. It was also the well-fitting Vieth–Sladek isotherm model among three-parameter isotherm models and its model exponent suggested that the adsorption data got in this research is more of Langmuir form rather than that of the Freundlich isotherm. Among the four-parameter isotherm models, most well-fitting isotherm was the Marczewski–Jaroniec isotherm and similarity was also seen between the $K_{MJ}$ and the Langmuir constant $K_L$.

The adjusted coefficient of determination ($\overline{R}^2$), which generally accounts for the number of variables and sample size in the model, is considered superior to the coefficient of determination ($R^2$), as it revises the overestimation by $R^2$. [82] It is more exact than $R^2$, specially when dealing with small samples.

On the basis of $\overline{R}^2$ values, the higher fitted model order among one and two parameter models in decreasing manner is shown in Table 8.

According to correlation coefficient $\overline{R}^2$ values, the fitness of the models for three, four and five parameter models is almost similar to each other. Thus, based on equivalent adsorption capacity, the orders followed by the models in decreasing manner are shown in Table 9.

Based on $\overline{R}^2$ values, the best-fitted model order among one and two parameter models is the Langmuir model with a maximum adsorption capacity of 1253 mg/g for As(III) and 1314 mg/g for As(V). Based on equivalent adsorption capacity values, the higher fitted model order among three, four and five parameter models is the Toth model with a maximum adsorption capacity of 1583 mg/g for As(III) and 2834 mg/g for As(V).

The descriptive models from the best to worst for As(III) and As(V) were sorted according to GoFM values and shown in Tables 10 and 11, respectively. Among 30 different isotherm models, the Vieth–Sladek isotherm was observed to be appropriate to predict the equilibrium data of adsorption of As(III) and As(V) on GAC/MnFe$_2$O$_4$ composite according to GoFM values, except Fritz–Schlunder–V was the best for As(III) on the basis of $R^2$ and SSE. But it signifies that the adsorption of both As(III) and As(V) do not form a multilayer on GAC/MnFe$_2$O$_4$ composite, it rather follows monolayer adsorption process and mechanism of adsorption process is complex.

4.10. Studies of influencing co-existing ions

The effect of concentrations of initial co-existing ions onto the adsorption process of As(III) and As(V) by GAC/MnFe$_2$O$_4$ composite is shown in Figures 15(a)–(c) and 16(a)–(c),
respectively. Results clearly showed that the % removal of As(III) and As(V) was observed
to decrease with the presence of a very low concentration of various ions such as copper
(Cu$^{2+}$), zinc (Zn$^{2+}$), bismuth (Bi$^{3+}$), lead (Pb$^{2+}$), cobalt (Co$^{2+}$), nickel (Ni$^{2+}$), chromium
(Cr$^{6+}$) and sulphate (SO$_{4}^{2-}$). However, in the presence of iron (Fe$^{3+}$) and cadmium (Cd$^{2+}$),
the removal efficiencies were observed to increase. The reduction in % removal in the
presence of Cu$^{2+}$, Zn$^{2+}$, Bi$^{3+}$, Pb$^{2+}$, Co$^{2+}$ and Ni$^{2+}$ ions may be explained on the basis of the
ionic radii. All these ions are bigger than As(III) and As(V) and therefore, in their presence
the % removal decreased.[35,83,84] This might be owing to the competition of these ions
with arsenic for the adsorption sites and/or owing to masking of adsorption sites by the
bigger ions.[85] Conversely, the ionic radii of Cd$^{2+}$ and Fe$^{3+}$ are almost the same; so, there
was no reducing effect.[85] The % removal of As(III) and As(V) increased in existence of
both Cd$^{2+}$ and Fe$^{3+}$ ions. Basically, Cd$^{2+}$ and Fe$^{3+}$ ions could be adsorbed by the adsorbent
and efficiently compensated the surface negative charge generated by specific adsorption of
As(III) and As(V) and acted as a bridge between the surface of adsorbent and As(III) and
As(V) ions, which has favoured the As(III) and As(V) anions adsorption.[42,83,84] While
the ionic radius of Cd$^{2+}$ is nearly the same, so, there was no reducing effect.[35] In addition
to this, Fe$^{3+}$ ions being an outstanding adsorbent for arsenic, the current influence in the
occurrence of Fe$^{3+}$ may also be because of the adsorption of arsenic on ferric hydroxides
(Fe(OH)$_{3}$) that would form while Fe$^{3+}$ ions are existing in wastewater under oxic conditions.
[86] Sulphate is divalent oxyanion and has competition with anions of both As(III) and
As(V) through enhanced electrostatic interaction.[87] Sulphate had an insignificant effect
on As(III) and As(V) adsorption. This is due to the fact that the sulphate binding affinity
for the adsorbent is much weaker than arsenic.[42,88,89] These results are consistent with
other study.[17,90]
Table 10. Models ranked from the best to worst based on GoFM values for the adsorption of As(III).

| Reduced $\chi^2$ | SSE | $R$ | $R^2$ | $R^2$ | Root-MSE |
|------------------|-----|-----|-------|-------|----------|
| Vieth–Sladek     | Fritz–Schlunder-V | Vieth–Sladek | Fritz–Schlunder-V | Vieth–Sladek | Vieth–Sladek |
| Langmuir–Freundlich | Vieth–Sladek | Sips | Fritz–Schlunder-V | Sips | Langmuir–Freundlich |
| Sips             | Marczewski–Jaroniec | Sips | Hill | Sips | Sips |
| Hill             | Langmuir–Freundlich | Hill | Holl–Krich | Hill | Holl–Krich |
| Radke–Praunzit III | Baudu | Holl–Krich | Langmuir–Freundlich | Holl–Krich | Langmuir–Freundlich |
| Redlich–Petersen | Marczewski–Jaroniec | Marczewski–Jaroniec | Baudu | Marczewski–Jaroniec | Marczewski–Jaroniec |
| Jossens          | Baudu | Baudu | Redlich–Petersen | Baudu | Baudu |
| Fritz–Schlunder–III | Radke–Praunzit III | Radke–Praunzit III | Jossens | Radke–Praunzit III | Jossens |
| Radke–Praunzit II | Redlich–Petersen | Redlich–Petersen | Fritz–Schlunder–III | Redlich–Petersen | Fritz–Schlunder–III |
| Khan             | Jossens | Jossens | Radke–Praunzit II | Jossens | Radke–Praunzit II |
| Radke–Praunzit I | Fritz–Schlunder–III | Fritz–Schlunder–III | Radke–Praunzit II | Fritz–Schlunder–III | Radke–Praunzit II |
| Jovanovic–Freundlich | Radke–Praunzit II | Radke–Praunzit II | Radke–Praunzit III | Radke–Praunzit III | Radke–Praunzit III |
| Brouers–Sotolongo | Khan | Khan | Khan | Khan | Khan |
| Langmuir–Freundlich–Jovanovic | Radke–Praunzit I | Radke–Praunzit I | Radke–Praunzit I | Radke–Praunzit I | Radke–Praunzit I |
| Toth             | Fritz–Schlunder–IV | Fritz–Schlunder–IV | Fritz–Schlunder–IV | Fritz–Schlunder–IV | Fritz–Schlunder–IV |
| Marczewski–Jaroniec | Vangnovic–Freundlich | Vangnovic–Freundlich | Toth | Vangnovic–Freundlich | Toth |
| Baudu            | Brouers–Sotolongo | Brouers–Sotolongo | Vangnovic–Freundlich | Brouers–Sotolongo | Brouers–Sotolongo |
| Langmuir–Jovanovic | Langmuir–Freundlich–Jovanovic | Langmuir–Freundlich–Jovanovic | Langmuir–Freundlich–Jovanovic | Langmuir–Freundlich–Jovanovic | Langmuir–Freundlich–Jovanovic |
| Fritz–Schlunder–IV | Toth | Toth | Toth | Toth | Toth |
| Fritz–Schlunder–V | Langmuir–Jovanovic | Langmuir–Jovanovic | Langmuir–Jovanovic | Langmuir–Jovanovic | Langmuir–Jovanovic |
| Unilan           | Unilan | Unilan | Unilan | Unilan | Unilan |
| Langmuir         | Langmuir | Langmuir | Langmuir | Langmuir | Langmuir |
| Koble–Corrigan  | Koble–Corrigan | Koble–Corrigan | Koble–Corrigan | Koble–Corrigan | Koble–Corrigan |
| Jovanovic        | Jovanovic | Jovanovic | Jovanovic | Jovanovic | Jovanovic |
| Freundlich       | Freundlich | Freundlich | Freundlich | Freundlich | Freundlich |
| Activated sludge | Activated sludge | Activated sludge | Activated sludge | Activated sludge | Activated sludge |
| Temkin           | Temkin | Temkin | Temkin | Temkin | Temkin |
| Dubinin–Radushkevich | Dubinin–Radushkevich | Dubinin–Radushkevich | Dubinin–Radushkevich | Dubinin–Radushkevich | Dubinin–Radushkevich |
| Henry            | Henry | Henry | Henry | Henry | Henry |
Table 11. Models ranked from the best to worst based on GoFM values for the adsorption of As(V).

| Reduced $\chi^2$ | SSE | $R$ | $R^2$ | $\overline{R}^2$ | Root–MSE |
|------------------|-----|-----|-------|-------------------|----------|
| Vieth–Sladek     |      |     |       |                   |          |
| Khan             |      |     |       |                   |          |
| Radke–Prausnitz I |    |     |       |                   |          |
| Radke–Prausnitz II |   |     |       |                   |          |
| Redlich–Peterson |     |     |       |                   |          |
| Jossens          |     |     |       |                   |          |
| Fritz–Schlunder–III | |     |       |                   |          |
| Toth             |     |     |       |                   |          |
| Marczewski–Jaroniec |   |     |       |                   |          |
| Fritz–Schlunder–V |     |     |       |                   |          |
| Langmuir–Freundlich |   |     |       |                   |          |
| Holl–Krich       |     |     |       |                   |          |
| Sips             |     |     |       |                   |          |
| Hill             |     |     |       |                   |          |
| Langmuir–Freundlich–Jovanovic | |     |       |                   |          |
| Langmuir–Jovanovic |   |     |       |                   |          |
| Fritz–Schlunder–IV |   |     |       |                   |          |
| Baudu            |     |     |       |                   |          |
| Brouers–Sotolongo |   |     |       |                   |          |
| Jovanovic–Freundlich | |     |       |                   |          |
| Unilan           |     |     |       |                   |          |
| Langmuir         |     |     |       |                   |          |
| Koble–Corrigan   |     |     |       |                   |          |
| Freundlich       |     |     |       |                   |          |
| Activated sludge |     |     |       |                   |          |
| Jovanovic        |     |     |       |                   |          |
| Temkin           |     |     |       |                   |          |
| Dubinin–Radushkevich |   |     |       |                   |          |
| Henry            |     |     |       |                   |          |

4.11. Desorption studies

Desorption of adsorbed As(III) and As(V) from the arsenic-loaded composite was performed utilizing various concentrations of NaOH solution. The outcomes are shown in Figure 15.

Figure 15. Effect of co-existing ions (a) copper, zinc and sulphate (b) iron, cadmium and bismuth (c) lead, cobalt, nickel and chromium on the removal of As(III) (C₀: 50 mg/L; M: 1 g/L; pH: 7; t: 70 min; T: 30 °C).
Figure 16. Effect of co-existing ions (a) copper, zinc and sulphate (b) iron, cadmium and bismuth (c) lead, cobalt, nickel and chromium on the removal of As(V) ($C_0$: 50 mg/L; $M$: 1 g/L; pH: 4; $t$: 70 min; $T$: 30 °C).

Figure 17(a) and (b). It is understood that when the concentration of NaOH was about 0.05 M, the rate of desorption of As(III) and As(V) enhanced with the rise in alkalinity and grasped a maximal of 79.4 and 82.1%, respectively. Afterwards, the rate of desorption
reduced with further rise in alkalinity. The poor rate of desorption exposed that the As(III) and As(V) adsorption onto the GAC/MnFe₂O₄ composite is partially reversible, because of the strong adsorptive interactions between As(III) and As(V) and the surfaces of the composite. The surface hydroxyl groups became deprotonated and negatively charged at high pH, occasioning an efficient desorption of negatively charged arsenic species. Therefore, NaOH solution was used for desorption of the adsorbed arsenic from adsorbent.[91] Then, the main possible desorption reaction could be summarized as:

\[
\text{MeOH}^+ \cdots \text{AsO}_3^{3-} + \text{OH}^- \rightarrow \text{MeOH} + \text{AsO}_3^{2-} + \text{H}_2\text{O}
\]  

(20)
5. Conclusions

- In this research, GAC/MnFe$_2$O$_4$ composite, fruitfully synthesized using a coprecipitation method was used to scavenge As(III) and As(V) from synthetically prepared wastewater and showed high removal efficiency.
- The optimum pHs for As(III) and As(V) adsorption process with GAC/MnFe$_2$O$_4$ composite are 7.0 and 4.0, respectively.
- The optimum adsorbent dose and contact time, temperature for As(III) and As(V) adsorption are 1 g/L, 70 min and 30 °C, respectively.
- Effect of co-existing ions present in copper smelting wastewater has been observed. Cd$^{2+}$ and Fe$^{3+}$ ions present in copper smelting wastewater showed positive effect on adsorption of As(III) and As(V) by that adsorbent, while other ions such as Cu$^{2+}$, Zn$^2$, Bi$^{3+}$, Pb$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Cr$^{6+}$ and SO$_4^{2-}$ had negative impact on removal of As(III) and As(V) by that adsorbent.
- Adsorbed As(III) and As(V) could be efficiently desorbed by 0.05-M NaOH solution.
- By applying 30 different isotherm models and utilizing procedure of the nonlinear regression for curve fitting analysis (maximizing the correlation coefficients ($R$, $R^2$ and $\bar{R}^2$) and minimizing the error values (SSE, Reduced $\chi^2$ and Root-MSE)) to evaluate optimum parameter sets, the Vieth–Sladek isotherm was seen appropriate to predict the equilibrium data of adsorption of As(III) and As(V) on GAC/MnFe$_2$O$_4$ composite according to GoFM values, except Fritz–Schlunder–V is the best for As(III) on the basis of $R^2$ and SSE. But it signifies that the adsorption of both As(III) and As(V) do not form a multilayer on GAC/MnFe$_2$O$_4$ composite, it rather follows monolayer adsorption process.
- On the basis of $\bar{R}^2$ values, the highest fitted model order among one and two parameter models is the Langmuir model with a maximum adsorption capacity of 1253 mg/g for As(III) and 1314 mg/g for As(V).
- On the basis of equivalent adsorption capacity values, the higher fitted model order among three, four and five parameter models is the Toth model with a maximum adsorption capacity of 1583 mg/g for As(III) and 2834 mg/g for As(V).
• The GAC/MnFe$_2$O$_4$ composite, hybrid adsorbent has a potential application for the removal of arsenic in water treatment.

**Nomenclature**

- $A_E$: the energy of adsorption (kJ/mol)
- $A_{FS}$: Fritz–Schlunder-IV isotherm constant ($\text{((mg/g)(L/mg)}^{n_{FS}}$)
- $a_{FS}$: Fritz–Schlunder-IV model exponent
- $a_K$: Khan isotherm exponent
- $A_{KC}$: Koble–Corrigan parameters ($\text{((mg/g)(L/mg)}^{n_{KC}}$)
- $b_B$: Baudu isotherm constant (L/mg)
- $B_{FS}$: Fritz–Schlunder-IV isotherm constant ($\text{((L/mg)}^{b_{FS}}$)
- $b_{FS}$: Fritz–Schlunder-IV model exponent
- $b_j$: Jossens model exponent
- $b_K$: Khan isotherm constant (L/mg)
- $B_{KC}$: Koble–Corrigan parameters ($\text{((L/g)}^{n_{KC}}$)
- $b_{TE}$: Temkin isotherm constant corresponding to heat of adsorption (J/mol)
- $C_0$: initial concentration of arsenic in the solution (mg/L)
- $C_e$: equilibrium concentration of arsenic in the solution (mg/L)
- $E$: mean free energy (kJ/mol)
- $K_1$: Fritz–Schlunder-V equilibrium constant ($\text{((L/mg)}^{a_{FS}}$)
- $K_2$: Fritz–Schlunder-V equilibrium constant ($\text{((L/mg)}^{b_{FS}}$)
- $K_{BS}$: Brouers–Sotolongo isotherm constant ($\text{((mg/g)(L/mg)}^{1/a}$)
- $K_F$: Freundlich isotherm constant ($\text{((mg/g)(L/mg)}^{1/n_F}$)
- $K_{DR}$: Dubinin–Radushkevich isotherm constant or activity coefficient linked to mean adsorption energy (mol$^2$/kJ$^2$)
- $K_{FS}$: Fritz–Schlunder-III isotherm constant ($\text{((L/mg)}^{n_{FS}}$)
- $K_H$: Hill isotherm constant (L/g)
- $K_{HE}$: adsorption equilibrium constant known as Henry constant (L/g)
- $K_{HK}$: Holl–Krich isotherm constant ($\text{((L/mg)}^{n_{HK}}$)
- $K_L$: Langmuir isotherm constant signifying the affinity between the adsorbent and the adsorbate molecules relating the energy of adsorption (L/mg)
$K_{LJF}$  Langmuir–Freundlich–Jovanovic isotherm constant (L/mg)

$K_J$  Jossens isotherm constant ((mg/g)(L/mg))

$K_{JF}$  Jovanovic–Freundlich isotherm constant depends only on the temperature (L/mg)

$K_{JV}$  Jovanovic isotherm constant linked to the free energy of adsorption (L/g)

$K_L$  Langmuir isotherm constant (L/mg)

$K_{LF}$  Langmuir–Freundlich isotherm constant (L/mg)

$K_{LJ}$  Langmuir–Jovanovic isotherm constant (L/mg)

$K_m$  Activated sludge model constant (L/g)

$K_{MJ}$  Marczewski–Jaroniec isotherm constant (L/mg)

$K_{RP}$  Redlich–Peterson isotherm constant (L/g)

$K_{RPI}$  Radke–Prausnitz I isotherm constant (L/mg)

$K_{RPH}$  Radke–Prausnitz II isotherm constant (L/mg)

$K_{RPHII}$  Radke–Prausnitz III isotherm constant (L/mg)

$K_S$  Sips isotherm constant related to affinity constant (mg/L)$^{-1/m_S}$

$K_T$  Toth isotherm constant linked to affinity constant (L/mg)

$K_{TE}$  Temkin isotherm constant corresponding to the maximum binding energy (L/mg)

$K_U$  Unilan isotherm constant ((L/mg)$^{bHK}$)

$K_{VS}$  Vieth–Sladek isotherm constant (L/mg)

$J$  Jossens isotherm constant ((L/mg)$^{bJ}$)

$M$  mass of the adsorbent (dry) used (g)

$m_{LF}$  Langmuir–Freundlich model exponent or heterogeneity factor

$m_{MJ}$  Marczewski–Jaroniec model exponent

$m_{RPI}$  Radke–Prausnitz I model exponent

$m_{RPH}$  Radke–Prausnitz II model exponent

$m_{RPHII}$  Radke–Prausnitz III model exponent

$m_s$  Sips model exponent

$n$  the number of observations in the experimental study

$n_F$  Freundlich model exponent
$n_{FS}$ Fritz–Schlunder-III model exponent

$n_H$ Hill cooperativity coefficient

$n_{HK}$ Holl–Krich model exponent

$n_{JF}$ Jovanovic–Freundlich model exponent

$n_{LJ}$ Langmuir–Jovanovic model exponent

$n_{LJF}$ Langmuir–Freundlich–Jovanovic model exponent

$n_{KC}$ Koble–Corrigan parameters

$N_m$ Activated sludge model exponential constant

$n_{MJ}$ Marczewski–Jaroniec model exponent

$n_T$ Toth isotherm exponent, a measure of surface heterogeneity

$p$ the number of parameters to be determined

$q_e$ adsorption capacity or amount of arsenic adsorbed onto the surface of adsorbent at equilibrium (mg/g)

$q_{e,exp}$ the equilibrium adsorption capacity observed from the batch experiment (mg/g)

$q_{e,model}$ the prediction from the isotherm model corresponding to $C_e$ (mg/g)

$q_{mB}$ maximum monolayer adsorption capacity predicted by the Baudu isotherm (mg/g)

$q_{mBS}$ maximum monolayer adsorption capacity forecasted by the Brouers–Sotolongo isotherm (mg/g)

$q_{mDR}$ maximum monolayer adsorption capacity predicted by the Dubinin–Radushkevich isotherm (mg/g)

$q_{mFS}$ maximum monolayer adsorption capacity forecasted by the Fritz–Schlunder-III isotherm (mg/g)

$q_{mFS5}$ maximum monolayer adsorption capacity given by the Fritz–Schlunder-V isotherm (mg/g)

$q_{mH}$ maximum monolayer adsorption capacity predicted by the Hill isotherm (mg/g)

$q_{mHK}$ maximum monolayer adsorption capacity predicted by the Holl–Krich isotherm (mg/g)

$q_{mjF}$ maximum monolayer adsorption capacity predicted by the Jovanovic–Freundlich isotherm (mg/g)

$q_{mjV}$ maximum monolayer adsorption capacity predicted by the Jovanovic isotherm (mg/g)

$q_{mk}$ maximum monolayer adsorption capacity forecasted by the Khan isotherm (mg/g)
Maximum monolayer adsorption capacity predicted by the Langmuir isotherm (mg/g)

Maximum monolayer adsorption capacity predicted by the Langmuir–Freundlich isotherm (mg/g)

Maximum monolayer adsorption capacity predicted by the Langmuir–Freundlich–Jovanovic isotherm (mg/g)

Maximum monolayer adsorption capacity predicted by the Langmuir–Jovanovic isotherm (mg/g)

Maximum monolayer adsorption capacity forecasted by the Marczewski–Jaroniec isotherm (mg/g)

Maximum monolayer adsorption capacity predicted by the Sips isotherm (mg/g)

Maximum monolayer adsorption capacity forecasted by the Toth isotherm (mg/g)

Maximum monolayer adsorption capacity forecasted by the Unilan isotherm (mg/g)

Maximum monolayer adsorption capacity predicted by the Vieth–Sladek isotherm (mg/g)

Universal gas constant (8.314 J/mol K)

Removal efficiency

Separation factor or adsorption intensity

Unilan model exponent dependent on temperature describing the heterogeneity of the system

Absolute temperature (K)

Working volume of the solution (L)

Baudu model exponent

Baudu model exponent
Greek symbols

\(\alpha\)  
Brouers–Sotolongo model exponent

\(\alpha_{FS}\)  
Fritz–Schlunder-V model exponent

\(\alpha_{RP}\)  
Redlich–Peterson isotherm constant \((L/mg)^{\beta_{RP}}\)

\(\beta_{FS}\)  
Fritz–Schlunder-V model exponent

\(\beta_{RP}\)  
Redlich–Peterson model exponent

\(\beta_{VS}\)  
Vieth–Sladek equilibrium constant

\(\varepsilon\)  
Polanyi potential \((mol^2/kJ^2)\)

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Disclosure statement

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