

Impact of co-existing ions on arsenic remediation using green nano zero-valent iron supported on nanocellulose: A fractional factorial design study

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Abstract

This study focused on developing a novel adsorbent material of green nano zero-valent iron supported by nanocellulose (G-NZVI/NCC) from agricultural waste for the effective removal of arsenic. The adsorption isotherm for arsenite (As^{3+}) and arsenate (As^{5+}) on G-NZVI/NCC showed maximum capacities of 4.2123 and 4.9579 $\text{mg}\cdot\text{g}^{-1}$, respectively. The model indicated that As^{3+} forms a multilayer on a heterogeneous surface, while As^{5+} forms a monolayer on a homogeneous surface. The Gibbs free energy for the adsorption of As^{3+} and As^{5+} on G-NZVI/NCC from water demonstrates a non-spontaneous process at higher temperatures for As^{3+} , but it occurs spontaneously for As^{5+} . Furthermore, most previous studies have largely overlooked the influence of co-existing ions in water, or have investigated them individually. Consequently, this study aimed to simulate real-world conditions by examining the simultaneous effects of all relevant ions. This comprehensive approach is critical for the practical implementation of the system, and statistical principles are employed for data analysis and interpretation. However, surface water contains competing ions such as calcium (Ca^{2+}), phosphate (PO_4^{3-}), bicarbonate (HCO_3^-), chloride (Cl^-), and sulfate (SO_4^{2-}) that can interfere with arsenic adsorption. A 2^{5-2} fractional factorial design was used to systematically evaluate individual factors, significant parameters, and their interactions on arsenic removal efficiency. The results revealed that Ca^{2+} , PO_4^{3-} , and HCO_3^- play crucial roles in arsenic removal, with Ca^{2+} and PO_4^{3-} enhancing removal efficiency, while HCO_3^- exhibits inhibitory effects. Notably, high PO_4^{3-} concentrations unexpectedly enhanced arsenic removal compared to previous studies, attributed to the synergistic physical and chemical adsorption properties of iron oxide and hydroxide phases. Mechanistic analysis revealed that As^{5+} can substitute PO_4^{3-} in vivianite formation, creating a vivianite-symplectite solid solution ($\text{Fe}_3(\text{PO}_4)_2.7(\text{AsO}_4)_{0.3}\cdot 8\text{H}_2\text{O}$), providing new insights into arsenic immobilization mechanisms under realistic water chemistry conditions.

Keywords: Arsenic, Arsenite, Arsenate, Nanocellulose, Nano zero valent iron

1. Introduction

Water contamination with toxic elements poses significant threats to human health and ecosystems globally. Among various pollutants, arsenic stands out as one of the most concerning inorganic contaminants due to its high toxicity, mobility in aquatic environments, and carcinogenic properties, even at low concentrations [1]. In nature, the most predominant forms of arsenic are Arsenite (As^{3+}) and Arsenate (As^{5+}), with As^{3+} being more toxic than As^{5+} [2, 3]. There are several sources of human exposure to arsenic including sedimentary deposits, volcanic rocks, soils, geothermal regions, industrial discharges, and anthropogenic [2, 4]. In Southeast Asia, countries including Bangladesh, India, China, Nepal, Vietnam, Myanmar, and Thailand have a problem with arsenic contamination in the water [5-12]. In 2025, arsenic contamination was identified in the northern region of Thailand, with concentrations in various rivers ranging from 0.013 to 0.018 $\text{mg}\cdot\text{L}^{-1}$. The primary source of the contamination originates from the headwaters of the Kok River in Shan State, Myanmar, due to gold and heavy metal mining activities in the area. Hazardous chemicals, such as arsenic, are commonly used in the process of extracting metals from raw ore in the region [13, 14].

There are several technologies for arsenic removal, such as precipitation, ion exchange, and adsorption. However, these methods are typically effective only for removing As^{5+} but are not as efficient for removing As^{3+} [15-17]. Nevertheless, the development of new adsorbents and their application in the adsorption process have significantly improved the removal efficiency of both arsenic species [18]. Nano zero valent iron synthesized from mango peel extract is an alternative method because mangoes have been cultivated and consumed extensively around the world, and it has been widely utilized in the industrial processing of mango, which results in large quantities of mango waste, including the seed and peel [19, 20]. Moreover, polyphenols are an important component in the mango peel extract and play a key role in reducing agents, which transfer electrons to metal ions. Moreover, polyphenols can be biodegradable and highly soluble in water at ambient temperature. There are alcohol functional group molecules that could reduce

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the particle size, prevent agglomeration, and improve the stability of nanoparticles, though some particles still agglomerate [21-23]. An appropriate nanocomposite is required to decrease agglomeration and enhance the surface area of nano zero-valent iron, such as oxide composites [24], activated carbon [25], mesoporous carbon [26], carbon nanotubes [27], titanium, and nanocellulose.

Nanocellulose is a major candidate for nanocomposite applications and has been widely used to remove various toxic contaminants due to its large surface area, biocompatibility, and nontoxicity [28-32]. Pineapple crown leaf is one of the most common forms of agricultural waste generated from the pineapple plant. The upper crown of the pineapple fruit generates about 10–25% of its total weight [33]. The main components of pineapple crown leaf are carbohydrate polymers composed of cellulose, hemicellulose, and lignin. In pineapple crown leaf, cellulose, hemicellulose, lignin, and others are present in amounts of 79–83%, 19%, 5–15%, and 4–5%, respectively. Because they contain high cellulose components, pineapple crown leaves can be utilized to extract nanocellulose [34-36]. Nanocellulose has abundant functional groups (O-H) on the surface that can be used for several chemical surface modifications. Due to nanocellulose having a large specific surface area and comprehensive surface functionality, the functionalization of NZVI onto nanocellulose provides an attractive alternative to generating hybrid composites for arsenic remediation [30, 37-40]. Despite this progress, most of the aforementioned studies were conducted using synthetic wastewater, but have not explored the impact of co-existing ions in water on removal efficiency, which is a crucial factor for the practical application of these processes.

In surface water, different species of ions are present that may compete with arsenic for active sites on the surface of G-NZVI/NCC. According to a literature review, phosphate (PO_4^{3-}) has similar chemical properties to arsenate, which can decrease the performance of arsenic removal because it competes for the active site on G-NZVI/NCC. It has been reported that bicarbonate (HCO_3^-) can reduce the performance of arsenic removal, similar to the effect of phosphate (PO_4^{3-}), due to complex formation characteristics with the oxide surface adsorbent [41-43]. Increasing the positive charge on the adsorbent can improve arsenic removal efficiency, especially when Ca^{2+} is present in groundwater, as it promotes arsenic adsorption [44]. Additionally, sulphate (SO_4^{2-}) may improve the efficacy of arsenic removal, contingent upon its concentration and the specific experimental conditions [45-47]. Although studies have examined the effect of various ions on arsenic removal, most research focused on the impact of each ion individually. Consequently, there is a lack of research on the behavior of multiple ions when they exist simultaneously in water, a condition that is likely to have a different effect on arsenic removal.

This study aims to evaluate the effectiveness of arsenic adsorption in the presence of multi-component ion species, using eco-friendly nano-zero valent iron made from agricultural waste. Furthermore, it aims to examine the performance of arsenic removal in a multi-component ion species model based on the experiment for applications to real water. The experiments used a fractional factorial design (FFD) to evaluate multiple variables with an efficient number of experimental runs. The FFD can explain the effects of multiple variables, evaluating both the main factors and their interaction system. Additionally, FFD can effectively identify key variables and provide superior data interpretation. The FFD is 2^{k-p} , where k is the number of factors, and $1/2^p$ is the fraction of the full factorial 2^k . In this study, the variables are followed by the major ion species in groundwater. Ca^{2+} , PO_4^{3-} , SO_4^{2-} , HCO_3^- , and Cl^- were chosen and studied to evaluate their impact on arsenic removal.

2. Materials and methods

2.1 Chemicals

The As^{3+} and As^{5+} stock solutions were prepared from sodium meta arsenite (AsNaO_2 , 98%, Panreac Química S.L.U., Europe) and disodium hydrogen arsenate heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, $\geq 98.0\%$, Sigma-Aldrich, USA), respectively. The G-NZVI/NCC was synthesized from Iron (II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 99.5%, QR&C, New Zealand). Sodium hydroxide (NaOH , 99.0%, RCI Labscan, Thailand), hydrogen peroxide (H_2O_2 , 30%, Sigma Aldrich, USA), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot 7\text{H}_2\text{O}$, 99.5%, RCI Labscan, Thailand), hydrochloric acid (HCl , 37%, RCI Labscan, Thailand), and potassium chloride (KCl , 99%, RCI Labscan, Thailand) were used to isolate nanocellulose from pineapple crown leaves. The ion species for the effect of ions experimental were prepared from sodium sulfate anhydrous (Na_2SO_4 , 99%, RCI Labscan, Thailand), calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 99%, RCI Labscan, Thailand), sodium hydrogen carbonate (NaHCO_3 , 99.5%, RCI Labscan, Thailand), sodium chloride (NaCl , 99%, Merck, Germany), and di-sodium hydrogen phosphate anhydrous (Na_2HPO_4 , 99%, RCI Labscan, Thailand).

2.2 Isolation of nanocellulose

Pineapple crown leaves (PCL) were prepared thoroughly by washing them multiple times with distilled water to eliminate impurities. The PCL were dried in a hot air oven at 60 °C until desiccated and then ground into fine powder. For the alkaline pretreatment, PCL were pretreated using 1 M of NaOH and stirred at 80 °C for 1 h. In the next step, the samples were allowed to cool to room temperature and rinsed with deionized water until a neutral pH was achieved. The samples were dried in a hot air oven at 60 °C until all the moisture had evaporated. Next, a bleaching process was conducted under 1 M of H_2O_2 for 1 h to remove residual lignin in pineapple leaves. The cellulose was dried in a hot air oven at 60 °C until all the moisture evaporated. The cellulose was then redispersed in deionized water and stirred until evenly dispersed. Acid hydrolysis was used to isolate nanocellulose. The pineapple crown leaf powder was hydrolyzed at 45 °C for 3 h with 2 M citric acid and 0.5 M HCl . To achieve a neutral pH of nanocellulose, the nanocellulose was washed with 0.5% of KCl solution. The residual KCl on the nanocellulose surface was removed by using ethanol. Drying nanocellulose was carried out in a hot air oven at 60 °C for 24 h.

2.3 Green nano zero valent iron supported on nanocellulose synthesis

G-NZVI/NCC was synthesized according to the procedure used by [38]. The nanocellulose was immersed in distilled water under stirring until the particles dispersed. In the next step, nanocellulose was immersed in 1 M of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ aqueous solution under stirring for 1 h. The mango peel extract, at a concentration of 50 $\text{g} \cdot \text{L}^{-1}$, was introduced into the $\text{NCC-FeSO}_4 \cdot 7\text{H}_2\text{O}$ aqueous solution at a steady rate of 5 $\text{mL} \cdot \text{min}^{-1}$, while the mixture was stirred using an agitator machine set to 300 rpm. Ferrous iron was reduced by the polyphenol in the mango peel extract, according to Equation (1):



At the end of the reaction, the appearance of black color on nanocellulose indicated the successful synthesis of G-NZVI on its surface. The G-NZVI/NCC was filtered from the aqueous solution using a suction pump with filter paper. Subsequently, the G-NZVI/NCC composite was dried in a vacuum oven at 50 °C until the weight was constant, after which it was stored for further analysis. The G-NZVI/NCC was analyzed for surface morphology and size by transmission electron microscopy (TEM, JEOL, JEM-2100 Plus, Japan). A zeta potential analyzer (Malvern, Zetasizer Nano ZS, England) was used to analyze the point of zero charge at several pH values on the G-NZVI/NCC surface.

2.4 Adsorption of arsenic on G-NZVI/NCC experiment

2.4.1 Adsorption kinetics experiment

The initial concentrations of As^{3+} and As^{5+} were set at $2 \text{ mg} \cdot \text{L}^{-1}$ and a reaction time of over 1440 min, using a G-NZVI/NCC dosage of $1 \text{ g} \cdot \text{L}^{-1}$ for the adsorption kinetics experiment. The samples were filtered using a $0.45 \text{ } \mu\text{m}$ filter, and the residual arsenic concentration was analyzed using ICP-OES. The kinetics adsorption study applied pseudo-first-order, pseudo-second order, and intraparticle diffusion models to study the rate of the adsorption process and identify the reaction-limiting step, according to Equations (2)–(4).

Pseudo-first order model:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

Pseudo-second order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

Where q_e represents the adsorption capacity of the adsorbent at equilibrium ($\text{mg} \cdot \text{g}^{-1}$), and q_t is the amount of adsorbate absorbed on the adsorbent surface at the time ($\text{mg} \cdot \text{L}^{-1}$), while k_1 and k_2 are the rate constants.

Weber-Morris Intraparticle diffusion model:

$$q_t = k_i t^{0.5} + c \quad (4)$$

Where k_i is the intraparticle diffusion rate constant ($\text{mg} \cdot \text{g}^{-1} \text{min}^{-0.5}$), and c is the boundary layer thickness or surface adsorption.

2.4.2 Adsorption isotherm experiment

The adsorption isotherm experiment was carried out with the concentrations of As^{3+} and As^{5+} ranging from 3.0 to $10.0 \text{ mg} \cdot \text{L}^{-1}$ for 600 min. The temperature was maintained at $303 \pm 1 \text{ K}$. 0.05 g of G-NZVI/NCC was added to a 50 mL polyethylene tube containing 50 mL of initial As^{3+} and As^{5+} solution. Samples were collected at equilibrium and filtered through a $0.45 \text{ } \mu\text{m}$ filter. The residual arsenate concentration resulting from the adsorption process was determined using ICP-OES. The Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin isotherm models were used to describe the adsorption process, its mechanism, and adsorption efficiency according to Equations (5)–(8):

Langmuir isotherm model:

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (5)$$

Freundlich isotherm model:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

Dubinin -Radushkevich isotherm model:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (7)$$

Temkin isotherm model:

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \quad (8)$$

2.5 Batch test

The experiment was conducted via an FFD with 2^{5-2} to evaluate the ion species that may have a significant effect on arsenic removal in this study. The experiment design included two value levels, with all possible combinations of five variables shown in Table 1. In this study, the initial arsenic concentration was consistently maintained at $2 \text{ mg} \cdot \text{L}^{-1}$. The low (–) and high (+) concentrations for alien ion species were controlled as follows: Ca^{2+} 20, 200 $\text{mg} \cdot \text{L}^{-1}$, HCO_3^- 50, 500 $\text{mg} \cdot \text{L}^{-1}$, SO_4^{2-} 20, 200 $\text{mg} \cdot \text{L}^{-1}$, PO_4^{3-} 1, 5 $\text{mg} \cdot \text{L}^{-1}$, and Cl^- 50, 500 $\text{mg} \cdot \text{L}^{-1}$. The concentration of alien ions was chosen to have a lower and a higher value, as follows

in natural waters. The 50 mL polyethylene centrifuge tubes contained 30 mL of arsenic solution, and the G-NZVI/NCC 0.03 g was added. The samples were collected with a syringe and filtered through a 0.45 μm membrane at 600 min. Samples were kept in a refrigerator to determine arsenic by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis.

Table 1 Design experiment of 2^{5-2}

Run number	Factors and codes				
	Ca^{2+} (A)	SO_4^{2-} (B)	PO_4^{3-} (C)	Cl^- (D = AB)	HCO_3^- (E = AC)
1	-	-	+	-	+
2	+	+	-	-	+
3	+	-	+	+	-
4	-	+	+	+	+
5	+	-	-	-	-
6	-	-	+	+	-
7	-	+	+	-	-
8	-	+	+	-	-
9	+	-	-	-	-
10	-	-	-	+	+
11	+	-	-	-	-
12	+	+	-	+	-
13	+	+	+	+	+
14	+	-	-	+	+
15	+	-	+	-	+
16	-	+	-	-	+
17	-	+	-	-	+
18	+	+	+	+	+
19	-	+	+	-	-
20	-	-	-	+	+
21	+	-	+	-	+
22	+	+	-	+	-
23	+	+	-	+	-
24	-	-	+	+	-

Notes: (1) The minus (-) and plus (+) signs demonstrate the low and high levels of the factors as follows: A (20,200); B (20,200); C (1,5); D (20,200); E (50,500). (2) The test level is $\text{mg}\cdot\text{L}^{-1}$.

2.6 Design of experiment (DOE)

The DOE is a statistical method used to analyze variable data about a specific research problem [48]. There are several types of DOE, including 2^k Full Factorial design, 2^{k-q} Fractional Factorial design, Response Surface Methodology, and Taguchi. DOE refers to the impact of independent or input variables (factors) on dependent or output variables (response). This experiment used an FFD for data analysis because it involves a significant number of variables, allowing for a reduction in the number of experiments required. FFD is a subset of experimental conditions in a Full Factorial Design. This method reduces the number of experiments, making it more cost-effective since it minimizes the number of experiments required. This experiment was conducted through 2^{5-2} using FFD with resolution III for data analysis. The experimental designs using the FFD for each species are displayed in Table 1. The minus (-) and plus (+) signs represent the low and high levels of the factors as follows: A (20, 200); B (20, 200); C (1,5); D (20, 200); E (50, 500). The principle of this experiment analysis is that the generator employment for each run is displayed in the second row. For example, in Run 1, variables A and B are assigned plus (+) and minus (-) signs, respectively. Consequently, variable D ($A \times B$) will have a minus sign (-) since it results from the simple multiplication of a plus and a minus sign. The same approach is applied to identify the sign of the variable E ($A \times C$). All experiments were replicated to ensure high-quality data with reliable and reproducible results.

3. Results and discussion

3.1 Characterization

For the zeta potential result of G-NZVI/NCC, as presented in Figure 1a, the point of zero charge (PZC) values of G-NZVI was found to be 1.25. The PZC values indicate that the surface of the material becomes positively charged when the pH drops below 1.25. As the pH rises above the PZC, the surface charge becomes more negative, indicating a shift in the surface properties of the materials. The transmission electron microscopy (TEM) image of G-NZVI/NCC, shown in Figure 1(b), reveals a predominantly spherical morphology with some irregular shapes. Additionally, the dispersion and particle size of G-NZVI/NCC effectively adhered to the NCC surface.

3.2 Effect of arsenic adsorption rate versus time

The experiment was conducted with an initial arsenic concentration of $2 \text{ mg}\cdot\text{L}^{-1}$ added to deionized water to study the effect of arsenic adsorption over time. The adsorption rates of both As^{3+} and As^{5+} in the deionized water system, as shown in Figure 2a, were higher than those in the synthesized ionic species water. This increase is attributable to the absence of competition between ionic species and arsenic for adsorption sites on the surface of G-NZVI/NCC [44, 48]. Another reason could be attributed to the low pH in the deionized water system, as presented in Figure 2b. The G-NZVI/NCC demonstrates a strong affinity for arsenic adsorption because the positively charged surface of G-NZVI/NCC creates electrostatic attraction with H_3AsO_4 and H_2AsO_4^- [49, 50]. In

contrast, the pH value of the synthesized ionic species in water consistently increased during all adsorption reactions. This increase was due to the production of hydroxide ions (OH^-) from the G-NZVI/NCC reaction in water and bicarbonate ions (HCO_3^-) acting as an alkaline buffer. These factors contributed to a rise in both the pH and alkalinity of the water [51]. Another reason could be the presence of low dissolved oxygen (DO) in synthesized ionic species, which inhibits the oxidation of G-NZVI/NCC to iron oxyhydroxide species, thereby limiting the effective adsorptive removal of arsenic, as shown in Figure 2c [45]. Also, in an anoxic condition, the DO value decreases, and the oxidation-reduction potential (ORP) value decreases as well (Figure 2d).

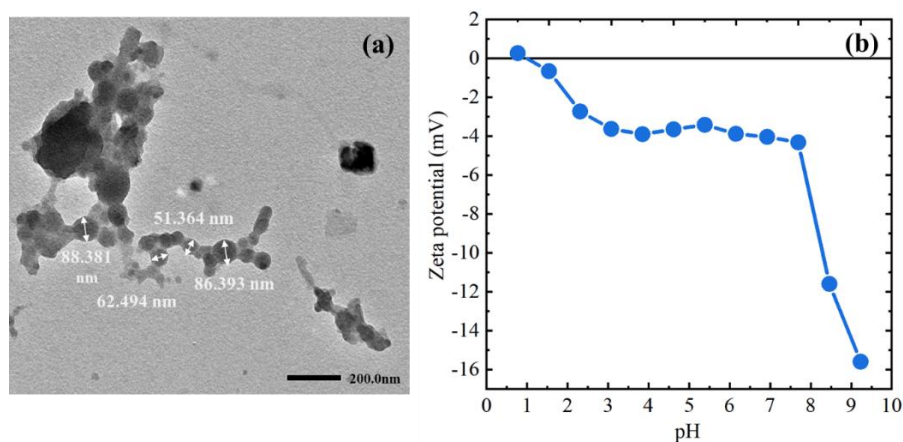


Figure 1 Characterization of G-NZVI/NCC (a) TEM image and (b) zeta potential versus pH

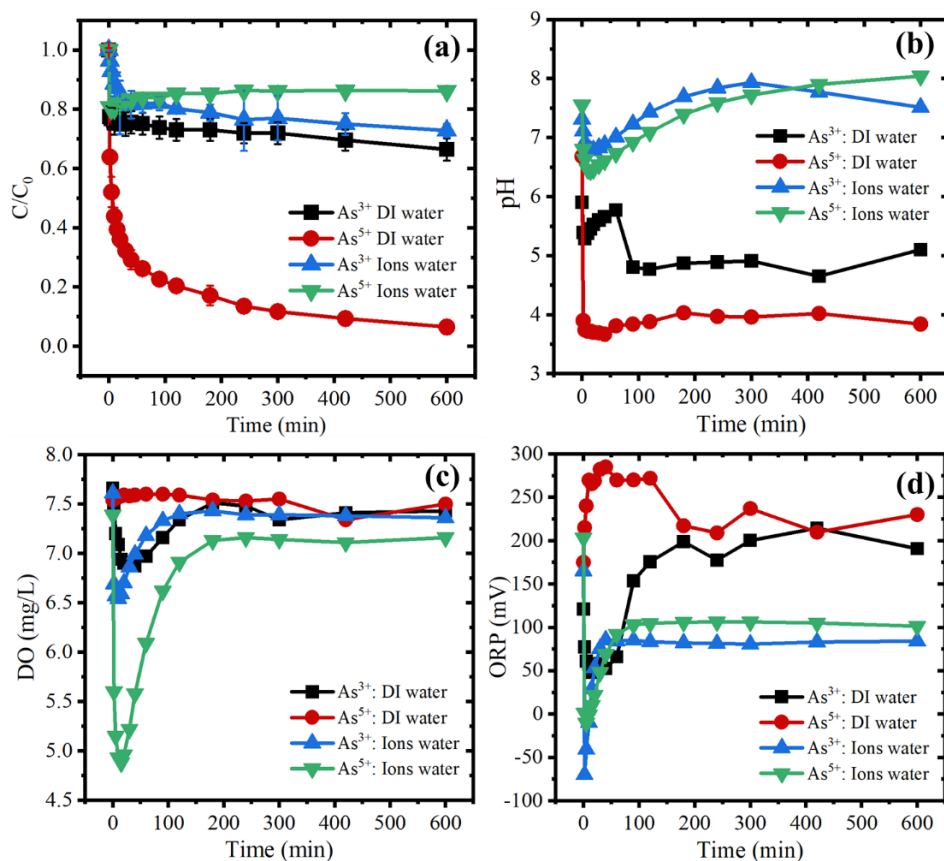


Figure 2 Arsenic removal by G-NZVI/NCC in deionized water and ion water system: (a) effect of concentration (b), effect of pH (c), effect of DO, and (d) effect of ORP

3.3 Adsorption kinetics and mechanism of As^{3+} and As^{5+} adsorption on G-NZVI/NCC

The adsorption kinetics of As^{3+} and As^{5+} removal using G-NZVI/NCC, as shown in Figure 2a, reveal that the adsorption rate of As^{3+} increased gradually, reaching near equilibrium after approximately 240 min. In contrast, As^{5+} adsorption increased rapidly within 40 min and approached equilibrium at approximately 420 min. The faster adsorption of As^{5+} compared to As^{3+} is because As^{3+} is neutral at natural pH, making it more soluble, mobile, and harder to remove [52]. The adsorption mechanism was divided into 3 mass transfer steps: external or boundary layer diffusion (film diffusion), internal or intraparticle diffusion, and finally adsorption onto active sites at the equilibrium stage. The pseudo-first order, pseudo-second order, and Weber-Morris intraparticle diffusion models were employed to study the rate of the adsorption process and mechanism, with the kinetic results for As^{3+} and As^{5+} shown in

Figure S1a–b and summarized in Table S1. The correlation coefficient (R^2) of the pseudo-second order model was higher than that of other models, which indicated that the rate-limiting process in As^{3+} and As^{5+} adsorption on G-NZVI/NC is the adsorption on active sites. Moreover, these results suggest that the adsorption of As^{3+} and As^{5+} depends on their concentration due to the high surface area of G-NZVI/NCC. The linear stages of the Weber-Morris Intraparticle Diffusion Model represent diffusion controls and limit the rate of As^{3+} and As^{5+} adsorption on G-NZVI/NCC. As shown in Table S1 and Figure S1c, all three stages of the linear line graph of intraparticle do not pass through (0,0), and the adsorption is controlled by multiple mechanisms [53]. The rate constant values (k_1 , k_2 , k_3) for As^{3+} adsorption are 0.0082, 0.015, and $0.0067 \text{ mg} \cdot \text{g}^{-1} \cdot \text{min}^{1/2}$, while the rate constant values for As^{5+} adsorption are 0.1823, 0.0753, and $0.0264 \text{ mg} \cdot \text{g}^{-1} \cdot \text{min}^{1/2}$. For both As^{3+} and As^{5+} , the lowest k_3 values suggest that intraparticle diffusion is not the rate-controlling step, but rather the adsorption steps themselves control the rate. In the first stage of the linear plot (1), As^{3+} and As^{5+} transfer through the liquid film around the G-NZVI/NCC via external diffusion. In the second stage of the linear plot (2), they diffuse into the pores of the G-NZVI/NCC, indicating internal diffusion. They adsorb into the active sites of G-NZVI/NCC, which is represented in the third stage (3). As^{3+} and As^{5+} were removed through a coprecipitation process, as Fe^{2+} dissolved and transformed into Fe_3O_4 , which easily coprecipitated with arsenic at a pH of 5.5–6.0 [54]. Additionally, FeOOH formed from the dehydration of $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ can adsorb arsenic onto the G-NZVI/NCC surface through inner-sphere or outer-sphere complexes [38, 54, 55].

3.4 Adsorption isotherm

Figure S2 shows the adsorption of As^{3+} and As^{5+} by G-NZVI/NCC. The Langmuir model, Freundlich model, Dubinin-Radushkevich model, and Temkin isotherm model are used to describe the adsorption process, its mechanism, and adsorption efficiency from liquid to solid phases. The adsorption results for As^{3+} and As^{5+} fit well with the Freundlich ($R^2 = 0.9946$) and Langmuir isotherm models ($R^2 = 0.9707$), respectively, and the adsorption constant is shown in Table S2. The adsorption isotherm results reveal that As^{3+} undergoes multilayer adsorption on a heterogeneous surface with an adsorption capacity of $4.2123 \text{ mg} \cdot \text{g}^{-1}$ on G-NZVI/NCC, while As^{5+} exhibits monolayer adsorption on a homogeneous surface with a capacity of $4.9579 \text{ mg} \cdot \text{g}^{-1}$. This results in a higher adsorption capacity compared to previous adsorbents, such as nano iron (hydr)oxide-impregnated granulated activated carbon with an arsenate adsorption capacity of $0.263 \text{ mg} \cdot \text{g}^{-1}$ [56] and NZVI with an arsenite adsorption capacity of $3.5 \text{ mg} \cdot \text{g}^{-1}$ [57]. The adsorption energy calculated from the DR-Isotherm model and the Temkin models for As^{3+} and As^{5+} adsorption were 0.5000 and $2.8524 \text{ KJ} \cdot \text{mol}^{-1}$ and 2.8867 and $2.9130 \text{ KJ} \cdot \text{mol}^{-1}$, respectively, revealing that the adsorption process of As^{3+} and As^{5+} on G-NZVI/NCC occurred via physisorption.

3.5 Effect of temperature and thermodynamics of As^{3+} and As^{5+} adsorption on G-NZVI/NCC

The effect of temperature was tested at 298, 318, and 328 K, as shown in Figure S3. As the temperature increased from 298 K to 328 K, the efficiency of As^{3+} and As^{5+} dropped. The thermodynamics were examined to determine whether adsorption occurred spontaneously, the effect of temperature, and whether the process was physisorption or chemisorption. The thermodynamic parameters, including Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), were calculated using Equations (9)–(10).

$$\Delta G^\circ = -RT \ln k_d \quad (9)$$

$$K_d = q_e / C_e \quad (10)$$

Van't Hoff equation (11)

$$\ln k_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

Where R is the gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), T is the temperature in Kelvin (K), and k_d is the thermodynamic equilibrium constant of the reaction process ($\text{L} \cdot \text{g}^{-1}$). The values of ΔH° ($\text{J} \cdot \text{mol}^{-1}$) and ΔS° ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) are calculated from the slope and intercept of Van't Hoff plots. Figure S4 shows thermodynamic plots of the relationship between $\ln k_d$ and $100/T$ of (a) As^{3+} and (b) As^{5+} removal by G-NZVI/NCC, and the thermodynamic data are shown in Table S3. The values of ΔH° for As^{3+} and As^{5+} adsorption were -9.79 and $-162.17 \text{ J} \cdot \text{mol}^{-1}$, respectively. The negative ΔH° values for both As^{3+} and As^{5+} suggest an exothermic adsorption process, with arsenic adsorption efficiency dropping as the temperature increases. A positive Gibbs free energy (ΔG°) values for As^{3+} adsorption suggest that the process is non-spontaneous at higher temperatures, requiring external energy or more favorable conditions. In contrast, a negative Gibbs free energy (ΔG°) for As^{5+} adsorption indicates that the process is naturally spontaneous, with its spontaneity increasing as the temperature rises from 298 to 328 K. The negative entropy values (ΔS°) for both As^{3+} and As^{5+} adsorption indicate a decrease in randomness at the solid-liquid interface during the process, as arsenic molecules become attracted on the G-NZVI/NCC surface and form ordered surface complexes [58].

3.6 Arsenic removal with ion species in different concentrations

The investigation of the effects of ion species competition during arsenic removal in water examines five selected ion species with different levels of concentration, as shown in Table 1. From Figure 3a, it is apparent that high removal rates of As^{3+} and As^{5+} were achieved in Runs 1, 4, 13, 15, 18, and 21, whereas Runs 2, 10, 14, 16, 17, and 20 exhibited lower removal rates. All the runs were conducted with the same concentration levels of Ca^{2+} and PO_4^{3-} . Therefore, Ca^{2+} and PO_4^{3-} have both inhibitory and enhancing effects on the removal of As^{3+} and As^{5+} . High concentrations of Ca^{2+} and PO_4^{3-} lead to significant removal of As^{3+} and As^{5+} , while low concentrations of Ca^{2+} and PO_4^{3-} result in minimal removal of As^{3+} and As^{5+} . Analysis of the investigation of the effects of ion species competition during arsenic removal in water will be discussed in the results by the FFD. As evidenced by Figure 3b, the final pH of the solution values was shown to be less significant compared to the initial pH, suggesting that pH has no impact on arsenic removal in the ion species system.

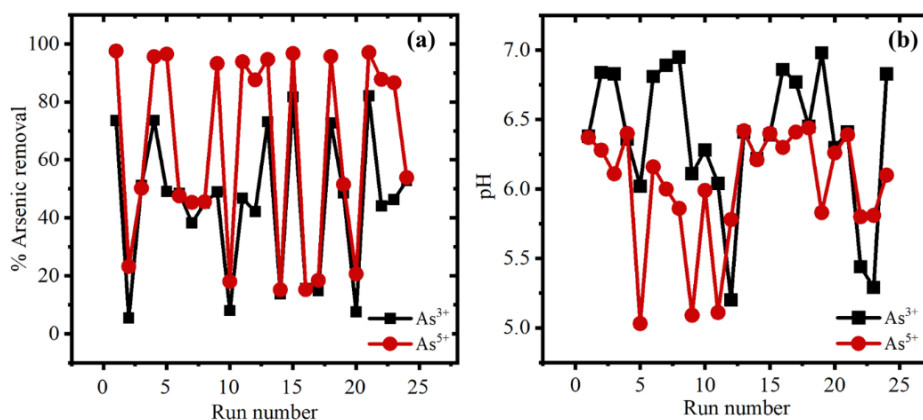


Figure 3 Effect of different concentrations of five selected species on (a) the removal of arsenic using G-NZVI/NCC, and (b) the final pH of the solution

3.6.1 Statistical analysis

The effect of ion species competition on arsenic removal in water by using G-NZVI/NCC was determined by FFD. Five selected ion species were investigated: Ca^{2+} , HCO_3^- , SO_4^{2-} , PO_4^{3-} , and Cl^- . According to Tables S4 and S5, the validity of the model was evaluated using statistical analysis through ANOVA [59]. The F-value determines the overall statistical significance of a regression equation, while the P-value assesses the significance of each coefficient. The F-values for the effects of ion species competition on As^{3+} and As^{5+} removal were 139.71 and 558.54, respectively. The observed p-value of 0.000 indicates that the model has a statistically significant effect. An analysis of the factors significant to the experiment shows a p-value of less than 0.05. (<0.05). The ANOVA analysis revealed that factors Ca^{2+} (A) and PO_4^{3-} (C) had a significant impact on As^{3+} removal, while factors Ca^{2+} (A), SO_4^{2-} (B), PO_4^{3-} (C), and HCO_3^- (E) were significant for As^{5+} removal, all with p-values below 0.05. The R^2 values were accurately predicted from the experimental data, showing 0.9839 and 0.9959 for the effects of ion species competition on the removal of As^{3+} and As^{5+} , respectively. This demonstrates that the method is a good fit and effectively explains the variation. In Table S6, the relationship between the factors and the percentage of arsenate removal may be established in the form of regression analysis, as shown in Equations (12) and (13).

$$Y_1 = 45.170 + 16.031X_1 - 1.844X_2 + 16.620X_3 - 0.657X_4 - 1.669X_5 - 1.369X_2X_3 + 0.907X_2X_5 \quad (12)$$

$$Y_2 = 63.665 + 29.917X_1 - 1.386X_2 + 8.954X_3 - 0.867X_4 - 6.315X_5 + 0.167X_2X_3 + 1.187X_2X_5 \quad (13)$$

where Y_1 and Y_2 represent the predicted percentage of As^{3+} and As^{5+} removed, respectively, and X_1 , X_2 , X_3 , X_4 , and X_5 represent Ca^{2+} , SO_4^{2-} , PO_4^{3-} , Cl^- , and HCO_3^- , respectively. The association between the factors and their corresponding response values was analyzed at a significance level (α) of 0.05 using a regression model. Tables S4 and S5 reveal that the model demonstrated a correlation coefficient of determination (R^2) exceeding 95% ($p = 0.005$), with several factors exceeding the significance [48, 60]. The R^2 between predicted values and experimental data is 95% ($p = 0.005$), with several factors exceeding the significance level, as presented in Tables S4 and S5. This result shows that the correlation coefficient between the predicted values, derived from equations 1 and 2, and the experimental data, presented in Figures 4(a) and 4(b) and Table S6, is established ($R^2 = 98.32\%$ and $R^2 = 99.59\%$). As demonstrated in Tables S4 and S5, Ca^{2+} , SO_4^{2-} , PO_4^{3-} , and HCO_3^- had a p-value of <0.05, indicating they were the most significant ions affecting the removal of both As^{3+} and As^{5+} in water. In contrast, Cl^- was determined to be an insignificant ion in the removal of both As^{3+} and As^{5+} from water (p-value = 0.392 and 0.109, respectively).

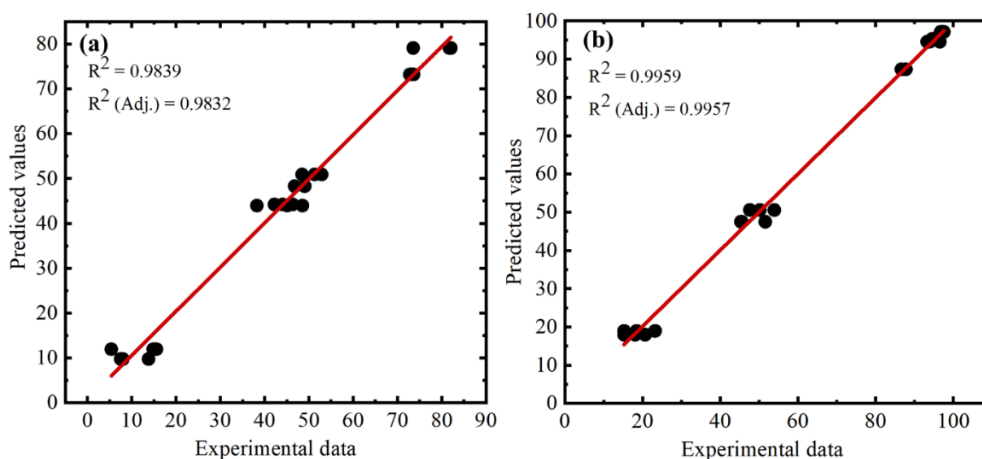


Figure 4 The percentage of (a) As^{3+} and (b) As^{5+} removal plot of predicted values versus experimental data (G-NZVI/NCC dosage = $1 \text{ g} \cdot \text{L}^{-1}$, $[\text{As}^{3+}]$ and $[\text{As}^{5+}] = 2.0 \text{ mg} \cdot \text{L}^{-1}$, pH initial 6.0 ± 0.5 , and sampling time = 600 min)

3.6.2 Main effect of ion species

The main effects plot illustrating the percentage removal of As^{3+} and As^{5+} from water is shown in Figure 5. The estimated effects for each factor, as shown in Figure 6, reveal positive main effect values of 32.06 and 33.24 for A (Ca^{2+}) and C (PO_4^{3-}) on As^{3+} , and 59.83 and 17.91 on As^{5+} , respectively. This indicates that these main factors significantly contribute to the enhancement of arsenic removal. The higher concentration of Ca^{2+} and PO_4^{3-} demonstrates the highest percentage of removal of both As^{3+} and As^{5+} from water. The enhancement of arsenic adsorption in the presence of Ca^{2+} can be attributed to two main reasons. First, Ca^{2+} may lead to the formation of insoluble $\text{Ca}_3(\text{AsO}_4)_2$ [61]. Second, Ca^{2+} can neutralize the negative charge of the G-NZVI/NCC surface, creating a connection between the negatively charged As^{5+} and the surface of G-NZVI/NCC, as illustrated in Equations (14) and (15) [44, 47, 62].



Another ion that significantly competes with arsenic is phosphate (PO_4^{3-}), as it belongs to the same group in the periodic table and shares similar chemical properties [63, 64]. The effects of PO_4^{3-} on arsenic adsorption in water using G-NZVI/NCC, as shown in Figures 5a-b, reveal that increasing the concentration of PO_4^{3-} to $5 \text{ mg}\cdot\text{L}^{-1}$ enhances the adsorption of both As^{3+} and As^{5+} at low initial pH. This finding contrasts with previous studies, as the low initial pH of the solution prevents the formation of complexes between Fe(III) and $\text{PO}_4^{3-}/\text{HPO}_4^{2-}$. Increasing the initial pH of the solution can lead to the formation of $\text{Fe}-\text{HPO}_4^{2-}$ adsorbed onto the surface of the adsorbent. Consequently, the number of active sites on the adsorbent decreases, reducing the adsorption of arsenic [47, 65]. Another reason is that high concentrations of PO_4^{3-} in water can lead to physical and chemical adsorption of iron oxide and hydroxide, resulting in the surface precipitation of PO_4^{3-} with iron as the crystalline form of vivianite ($\text{Fe}_3(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}$) [66-68]. It was demonstrated that vivianite could absorb 88% of As^{5+} from a solution with an initial concentration of $100 \mu\text{M}$. This occurs because As^{5+} can replace PO_4^{3-} in vivianite, forming the vivianite-symplectite solid solution ($\text{Fe}_3(\text{PO}_4)_2\cdot 7(\text{AsO}_4)_{0.3}\cdot 8\text{H}_2\text{O}$) [66].

Contrarily, the main factors B (SO_4^{2-}), D (Cl^-), and E (HCO_3^-) were shown to inhibit arsenic removal. The negative main effect estimates for B (SO_4^{2-}), D (Cl^-), and E (HCO_3^-) were -3.67 , -1.31 , and -3.34 for As^{3+} , and -2.71 , -1.74 , and -12.63 for As^{5+} . A low concentration of SO_4^{2-} ion was more effective at adsorbing both As^{3+} and As^{5+} compared to a high concentration. This increased effectiveness is because of the repulsion between sulfate ions and negatively charged arsenic species [69]. Additionally, SO_4^{2-} could replace iron hydroxide in the process, which led to a decrease in active sites on the iron surface available for arsenic adsorption [43, 70]. Regarding HCO_3^- , it plays an inhibiting role in arsenic removal. High concentrations of HCO_3^- in water decrease the efficiency of As^{3+} and As^{5+} adsorption on the G-NZVI/NCC surface because of the competition for adsorptive sites between HCO_3^- and arsenic species, which can be interference in adsorption processes. Furthermore, HCO_3^- can react with the inner-sphere surface complexes of iron hydroxide, leading to the formation of iron carbonate (FeCO_3) [71]. This reaction may contribute to the reduced performance observed in As^{3+} and As^{5+} . To conclude, among the studied species, the estimated positiveness in removing both As^{3+} and As^{5+} follows the order $\text{Ca}^{2+} > \text{PO}_4^{3-}$, whereas the estimated negative effects follow the order $\text{HCO}_3^- > \text{SO}_4^{2-}$. In the case of Cl^- , no significant change was observed.

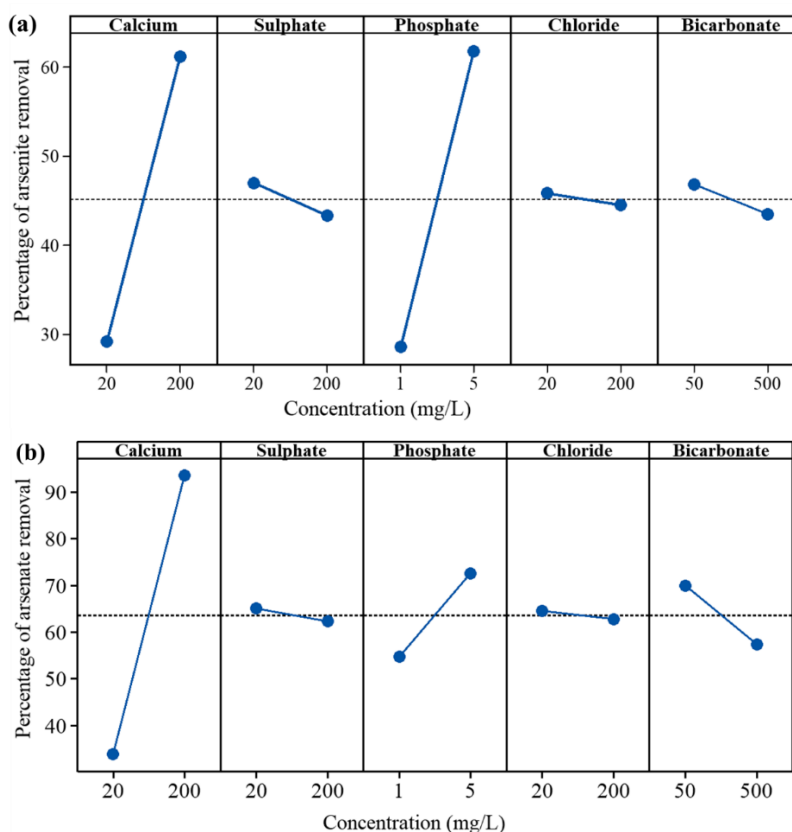


Figure 5 Main effect of five selected species on arsenic removal by G-NZVI/NCC of (a) As^{3+} and (b) As^{5+}

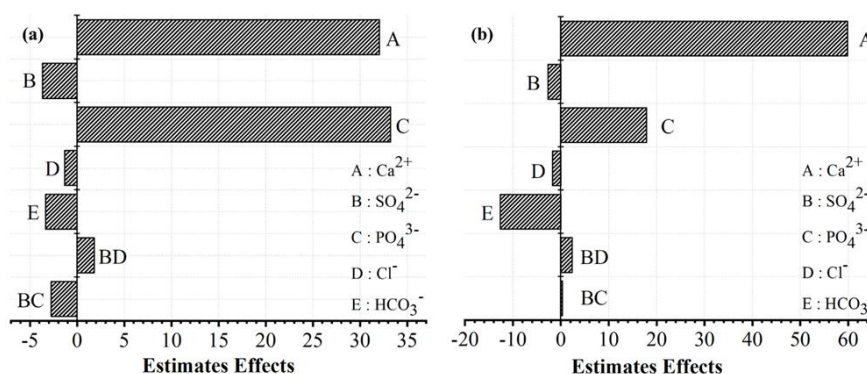


Figure 6 Estimated effects for five selected species of (a) As^{3+} and (b) As^{5+}

3.6.3 Effect of interaction factors

The effect of interaction species is examined because it helps to understand how the impact of one factor changes depending on the levels of other factors, as shown in Figure 6. The interaction of two factors indicates antagonism or synergism. As illustrated in Table 1, the design matrix displays interactions as cross-products. The plot of two-factor interactions, illustrating the percentage of arsenic removal for each interaction, is shown in Figure 7. The way factors interact plays a significant role in arsenic removal, especially when looking at the slope of each line in each cell based on the factor shown on the x-axis. Conversely, when the gap between the two data points (black and red) on the y-axis is significant, the interactions driven by factors on the y-axis become important, as shown in Figure 7 with factors A (Ca^{2+}) and E (HCO_3^-). The significant interaction factor affected by the removal of both As^{3+} and As^{5+} is AE ($\text{Ca}^{2+} \times \text{HCO}_3^-$), influencing the percentage of arsenic removal. Figure 7 illustrates that, among all cells of paired interaction factors, the blue lines (representing low levels) in columns B and D (Figure 7a) and columns B, D, and E (Figure 6b) exhibit slopes close to zero or horizontal. The data point overlaps (blue and red) are located in cells BD, CE, and BE (high E) in Figure 7a, as well as in BD, CE (low E), DE (low E), AE (low E), and BC (low c). By observing both horizontal lines and data point overlap, one can identify key factors influencing interactions within each cell.

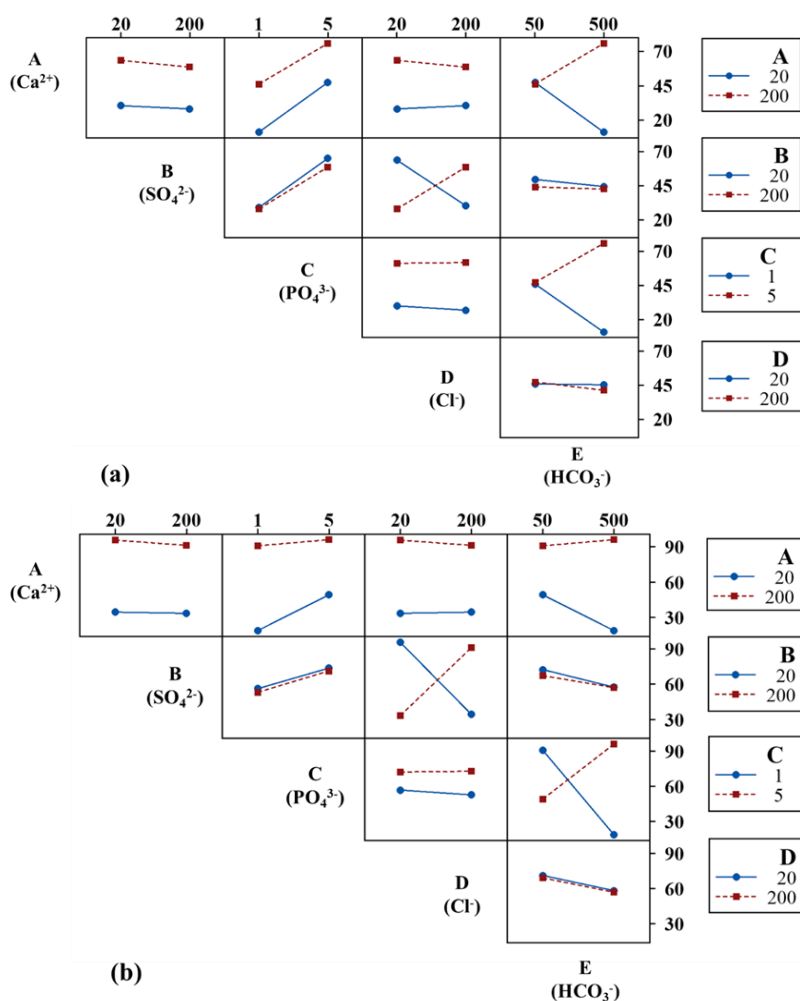


Figure 7 Effect of interaction factors in terms of (a) As^{3+} and (b) As^{5+} percentage removal

4. Conclusion

In this study, the adsorption of arsenite (As^{3+}) and arsenate (As^{5+}) on G-NZVI/NCC followed a pseudo-second-order kinetic model, with correlation coefficients (R^2) of 0.9951 and 0.9984, respectively, indicating that the adsorption was a rate-controlling step. The adsorption isotherm was applied, with the Freundlich and Langmuir models fitted to As^{3+} and As^{5+} adsorption on G-NZVI/NCC. The results indicated that As^{3+} forms a multilayer on a heterogeneous surface, while As^{5+} creates a monolayer on a homogeneous surface. According to the Langmuir isotherm, the maximum adsorption capacities were $4.2123 \text{ mg}\cdot\text{g}^{-1}$ for As^{3+} and $4.9579 \text{ mg}\cdot\text{g}^{-1}$ for As^{5+} . Furthermore, this study investigated how five different ion species affected the removal of arsenic using G-NZVI/NCC. The experiment followed the 2^{5-2} fractional factorial design with resolution III. As a result, Ca^{2+} , PO_4^{3-} , and HCO_3^- are key species that significantly contribute to arsenic removal. In both systems, Ca^{2+} and PO_4^{3-} improve arsenic removal, while HCO_3^- reduces arsenic removal. The FFD results indicate that the best conditions for arsenic removal in the experiment involve raising the levels of Ca^{2+} and PO_4^{3-} while lowering the level of HCO_3^- . Compared to previous studies, a high concentration of PO_4^{3-} in water could improve arsenic removal due to the physical and chemical adsorption of iron oxide and hydroxide. This process results in the surface precipitation of PO_4^{3-} with iron, forming vivianite ($\text{Fe}_3(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}$) in its crystalline state. Regeneration and multi-cycle reuse were not investigated. Because the Fe^0 phase of G-NZVI/NCC undergoes irreversible oxidation/aging and forms stable precipitates during adsorption, the material is expected to be used as a single-use sorbent; spent media should be managed as arsenic-bearing solid waste according to applicable regulations. Future studies should evaluate the performance of G-NZVI/NCC in real surface water and groundwater matrices.

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6. Author Contributions

Ratthiwa Deewan: conceptualization, data curation, formal analysis, investigation, methodology, validation, writing - original draft, writing - review & editing. Dickson Yuk-Shing Yan: conceptualization, data curation, formal analysis, investigation, methodology, validation, writing - review & editing. Pummarn Khamdagsag: conceptualization, writing - original draft, writing - review & editing. Visanu Tanboonchuy: conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, resources, supervision, validation, visualization, writing - original draft, writing - review & editing.

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8. Supporting Information

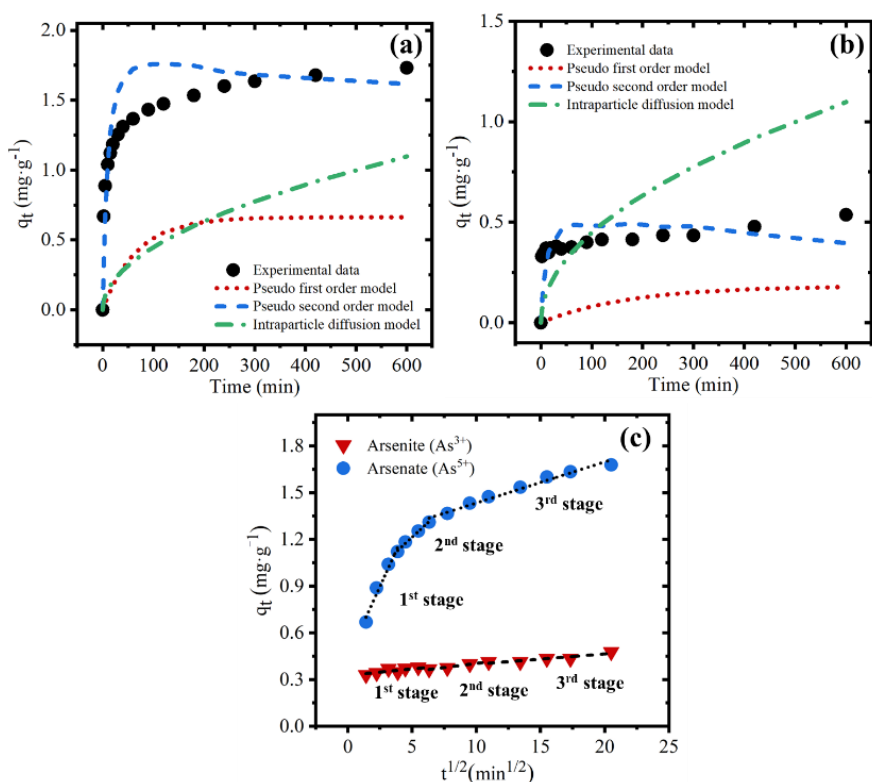


Figure S1 Nonlinear plots of Pseudo-first order, Pseudo-second order, Intraparticle models, and experimental data of adsorption kinetics (a) adsorption of As³⁺, (b) adsorption of As⁵⁺, and (c) Intraparticle diffusion model of As³⁺ and As⁵⁺ adsorption by G-NZVI/NCC (Conditions: initial concentration As³⁺ and As⁵⁺ of 2 mg·L⁻¹, G-NZVI/NCC dosage of 1 g·L⁻¹, and pH 6)

Table S1 Adsorption kinetic parameters for arsenic adsorption by G-NZVI/NCC

Kinetic models	Parameters	Arsenic species	
		Arsenite (As ³⁺)	Arsenate (As ⁵⁺)
Pseudo-first order	k ₁ (l·min ⁻¹)	0.0030	0.0070
	q _e (mg·g ⁻¹)	0.1840	0.6630
	R ²	0.9375	0.9440
Pseudo-second order	k ₂ (g·mg ⁻¹ ·min)	0.2520	0.0590
	q _e (mg·g ⁻¹)	0.4640	1.6870
	R ²	0.9951	0.9984
Intraparticle diffusion	k ₁ (mg·g ⁻¹ ·min ^{1/2})	0.0082	0.1823
	R ²	0.6279	0.9699
	k ₂ (mg·g ⁻¹ ·min ^{1/2})	0.0105	0.0758
	R ²	0.9795	0.9915
	k ₃ (mg·g ⁻¹ ·min ^{1/2})	0.0067	0.0264
	R ²	0.8578	0.9766

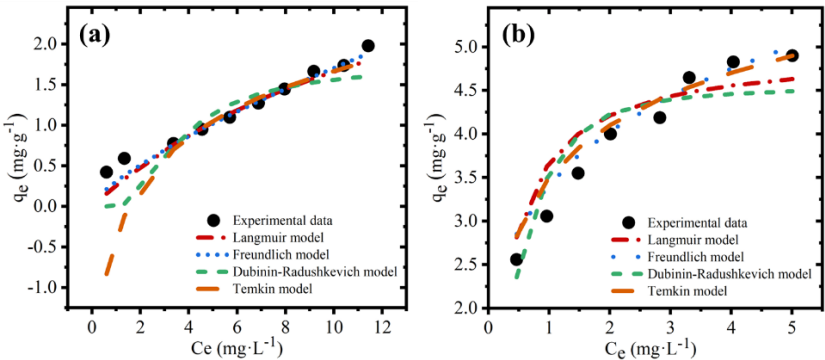


Figure S2 Nonlinear plots of Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin isotherm models showing (a) adsorption of As³⁺ and (b) adsorption of As⁵⁺ by G-NZVI/NCC

Table S2 Adsorption isotherm parameters for Arsenic adsorption by G-NZVI/NCC

Isotherm models	Parameters	Arsenic species	
		Arsenite (As ³⁺)	Arsenate (As ⁵⁺)
Langmuir model	K _L (l·min ⁻¹)	0.0653	2.8329
	q _m (mg·g ⁻¹)	4.2123	4.9579
	R ²	0.9903	0.9707
Freundlich model	K _F (g·mg ⁻¹ ·min)	0.3099	3.4205
	1/n	0.7410	0.2371
	R ²	0.9946	0.9703
Dubinin-Radushkevich model	K _D (mg·g ⁻¹ ·min ^{1/2})	2 x 10 ⁻⁶	6 x 10 ⁻⁸
	q _m (mg·g ⁻¹)	1.7542	4.5467
	E (kJ·mol ⁻¹)	0.5000	2.8867
	R ²	0.8989	0.9055
Temkin model	K _T	0.6536	55.5343
	b (kJ·mol ⁻¹)	2.8524	2.9130
	R ²	0.9722	0.9792

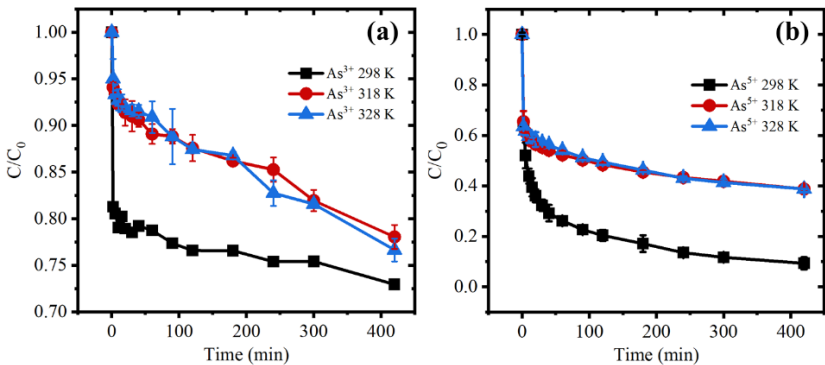
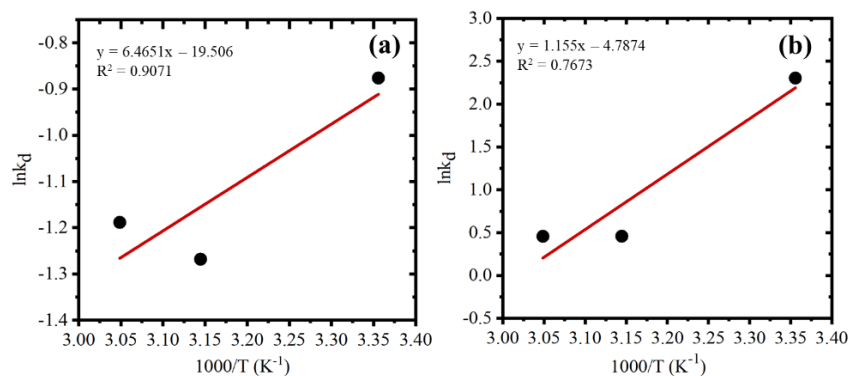


Figure S3 Effect of temperature on (a) As³⁺ and (b) As⁵⁺ removal by G-NZVI/NCC across a temperature range of 298–328 K (Conditions: Initial concentration As³⁺ and As⁵⁺ of 2 mg·L⁻¹, G-NZVI/NCC dosage of 1 g·L⁻¹, and pH 6)

Table S3 Thermodynamic parameters of As³⁺ and As⁵⁺ adsorption by G-NZVI/NCC

Arsenic species	Temperature (K)	ΔG° (kJ·mol ⁻¹)	ΔS° (J·mol ⁻¹ K ⁻¹)	ΔH° (J·mol ⁻¹)
Arsenite (As ³⁺)	298	2171.10	-39.77	-9.76
	318	3352.42		
	328	3241.05		
Arsenate (As ⁵⁺)	298	-5707.68	-19.51	-162.17
	318	-1211.39		
	328	-1246.28		

**Figure S4** Relationship between $\ln K_d$ and $100/T$ of (a) As³⁺ and (b) As⁵⁺ removal by G-NZVI/NCC (Conditions: Initial concentration As³⁺ and As⁵⁺ of 2 mg·L⁻¹, G-NZVI/NCC dosage of 1 g·L⁻¹, and pH 6)**Table S4** Variance analysis of the effect of ion species competition on aqueous arsenite removal

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	7	13020.5	1860.07	139.71	0.000
Linear	5	12955.8	2591.15	194.63	0.000
Calcium (A)	1	6167.6	6167.58	463.26	0.000
Sulphate (B)	1	81.6	81.59	6.13	0.025
Phosphate (C)	1	6629.4	6629.40	497.95	0.000
Chloride (D)	1	10.4	10.36	0.78	0.391
Bicarbonate (E)	1	66.8	66.84	5.02	0.040
2-way Interactions	2	64.7	32.34	2.43	0.120
Sulphate*Phosphate (BC)	1	45.0	44.96	3.38	0.085
Sulphate*Bicarbonate (BE)	1	19.7	19.72	1.48	0.241
Error	16	213.0	13.31		
Total	23	13233.5			

$R^2 = 98.39\%$ R^2 (adj.) = 97.69%

Table S5 Variance analysis of the effect of ion species competition on aqueous arsenate removal

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	7	24460.7	3494.4	558.54	0.000
Linear	5	24426.3	4885.3	780.86	0.000
Calcium (A)	1	21480.9	21480.9	3433.51	0.000
Sulphate (B)	1	46.1	46.1	7.37	0.015
Phosphate (C)	1	1924.0	1924.0	307.54	0.000
Chloride (D)	1	18.1	18.1	2.89	0.109
Bicarbonate (E)	1	957.1	957.1	152.99	0.000
2-way Interactions	2	34.5	17.2	2.76	0.094
Sulphate*Phosphate (BC)	1	0.7	0.7	0.11	0.748
Sulphate*Bicarbonate (BE)	1	33.8	33.8	5.40	0.034
Error	16	100.1	6.3		
Total	23	24560.8			

$R^2 = 99.59\%$ R^2 (adj.) = 99.41%

Table S6 2^{5-2} FFD matrix and comparison of experimental vs. predicted arsenic removal by G-NZVI/NCC

Run number	Factors and codes					As ³⁺ removal (%)		As ⁵⁺ removal (%)	
	Ca ²⁺ A	SO ₄ ²⁻ B	PO ₄ ³⁻ C	Cl ⁻ D = AB	HCO ₃ ⁻ E = AC	Exp. data	Pre. value	Exp. data	Pre. value
1	200	20	5	20	500	73.57	79.12	97.57	97.12
2	20	200	1	20	500	5.38	11.94	23.23	18.98
3	20	20	5	200	50	51.30	50.89	50.18	50.56
4	200	200	5	200	500	73.66	73.19	95.63	95.32
5	200	20	1	20	50	49.09	48.29	96.52	94.55
6	20	20	5	200	50	48.48	50.89	47.59	50.56
7	20	200	5	20	50	38.24	43.97	45.32	47.48
8	20	200	5	20	50	45.10	43.97	45.54	47.48
9	200	20	1	20	50	49.00	48.29	93.26	94.55
10	20	20	1	200	500	7.99	9.76	18.06	17.98
11	200	20	1	20	50	46.78	48.29	93.88	94.55
12	200	200	1	200	50	42.22	44.21	87.61	87.34
13	200	200	5	200	500	73.11	73.19	94.64	95.32
14	20	20	1	200	500	13.79	9.76	15.22	17.98
15	200	20	5	20	500	81.72	79.12	96.73	97.12
16	20	200	1	20	500	15.58	11.94	15.25	18.98
17	20	200	1	20	500	14.86	11.94	18.45	18.98
18	200	200	5	200	500	72.80	73.19	95.70	95.32
19	20	200	5	20	50	48.56	43.97	51.57	47.48
20	20	20	1	200	500	7.50	9.76	20.65	17.98
21	200	20	5	20	500	82.05	79.12	97.06	97.12
22	200	200	1	200	50	44.09	44.21	87.79	87.34
23	200	200	1	200	50	46.33	44.21	86.61	87.34
24	20	20	5	200	50	52.89	50.89	53.90	50.56

Notes: Exp. data = Experimental data; Pre. value = Predicted value