

Optimizing Arsenic Removal Using Surface-Modified Magnetic Nanoparticles via Taguchi Experimental Design

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Abstract

Humic acid (HA) was used to modify iron oxide magnetic nanoparticles ($\text{Fe}_3\text{O}_4/\text{HA}$ MNP) to improve adsorption efficiency for arsenic(V) (As(V)). The HA reduced the agglomeration of Fe_3O_4 MNP, which increased the specific surface area of the Fe_3O_4 MNP from 48.2 to 92.2 m^2/g . The optimal conditions for As(V) removal by $\text{Fe}_3\text{O}_4/\text{HA}$ MNP were determined via the Taguchi method, which were at pH 3, a Fe_3O_4 MNP/HA dosage of 5 g/L, adsorption time of 180 min, and concentration of coexisting ions of 20 mg/L. The highest As(V) removal efficiency of $\text{Fe}_3\text{O}_4/\text{HA}$ MNP was 94.3 %. The removal of As(V) by $\text{Fe}_3\text{O}_4/\text{HA}$ MNP followed pseudo-second-order kinetics, with an equilibrium adsorption capacity of 0.452 mg/g and a rate constant of 0.222 $\text{g}\cdot\text{min}/\text{mg}$. The elevated adsorption rate is ascribed to the relatively high $\text{Fe}_3\text{O}_4/\text{HA}$ MNP dosage relative to the initial As(V) concentration, which provided an excess of available active sites. As(V) uptake by $\text{Fe}_3\text{O}_4/\text{HA}$ MNP proceeds mainly via electrostatic interactions, ion exchange, and surface complexation with carboxyl and phenolic hydroxyl groups. Unlike previous HA-coated Fe_3O_4 systems, this study provides a systematic assessment of how pH, adsorbent dosage, contact time, and coexisting ions jointly control As(V) removal by $\text{Fe}_3\text{O}_4/\text{HA}$ MNP, offering practical guidance for process design under realistic multi-ion conditions.

Keywords: Arsenic(V) adsorption; Humic acid-coated Fe_3O_4 ; Coexisting ions; Taguchi optimization; Multi-ion matrix; Pseudo-second-order kinetics.

1. Introduction

Arsenic (As) is ranked as the 20th most abundant element in the Earth's crust, 14th in seawater, and 12th in the human body [1]. It can cause black foot disease [2], and cancer [3], and can affect the central nervous system [4]. Many countries are affected by As pollution in their natural underground waters [5]. In aqueous solutions, As occurs as As(III) and As(V) in arsenates and arsenates, respectively [6], with As(III) being more toxic than As(V) due to its higher solubility [7]. Conventional methods for As removal from the aqueous solutions are co-precipitation and coagulation with aluminium, iron, and lime, electrochemical treatment, ion exchange, and membrane filtration [8-10]. However, these methods tend to produce bulky wet sludge [11, 12].

Recent studies have focused on the adsorption of heavy metals by magnetic nanoparticles (MNP) because they offer the advantages such as low processing costs, high adsorption capacities, facile separation, and renewability [13, 14]. In the last decade, Fe₃O₄ MNP has gained popularity as the preferred MNP in water treatment technology due to its ease of separation from the solutions via magnetic field, reusability after separation, rapid sorption and reaction kinetics [15-18]. Haematite (α -Fe₂O₃) MNP could remove various heavy metals, such as Cr³⁺, Co²⁺, Ni²⁺, Cu²⁺, Cd²⁺, Pb²⁺ and As³⁺, as well as *Escherichia coli* from water with high adsorption capacities above 60 % [19, 20]. However, the efficiency of Fe₃O₄ MNP is often limited by instability of surface functional groups, and agglutination, leading to its decreased adsorption capacity [21, 22]. Recent reports have shown that humic acid (HA) enhances the stability of the surface functional groups and effective surface area of Fe₃O₄ (~35 %), which are critical features in promoting adsorption performance of Fe₃O₄ MNP (over 95 %) [23].

The Taguchi method is a well-established statistical design of experiments approach

that enables efficient optimization of multi-factor systems using orthogonal arrays. In environmental engineering, Taguchi designs have been widely used to identify influential factors and approximate optimal operating conditions with fewer experimental runs than conventional full factorial designs, while jointly considering mean responses and signal-to-noise (S/N) ratios [24, 25]. In the realm of product design, the Taguchi method stands out as a highly effective approach for simultaneously reducing product costs, enhancing quality, and shortening development timelines. Within environmental science, this method is recognized as a straightforward experimental design strategy that efficiently identifies optimal operating conditions with minimal experimentation [24]. Compared to other optimization techniques, the Taguchi method delivers expedited results through fewer trials. Notably, it is unique in determining optimal conditions by concurrently assessing both the mean responses and signal-to-noise (S/N) ratios, thereby offering a robust framework for performance evaluation [25].

Several studies have reported humic acid (HA)–modified Fe_3O_4 nanoparticles for arsenic removal; however, most of these investigations have been conducted at comparatively high As concentrations, under simplified ionic compositions, or without systematic optimization of operating conditions. In particular, the relative influence of pH, adsorbent dosage, contact time, and coexisting ions on As(V) uptake by HA-coated Fe_3O_4 under realistic multi-ion conditions has not been comprehensively quantified. Furthermore, although Taguchi designs have been applied in various environmental processes, their use to optimize As(V) adsorption by HA–modified magnetic nanoparticles (MNPs) in the presence of multiple competing ions remains limited. Addressing these gaps is essential for translating HA-coated Fe_3O_4 from laboratory proof-of-concept towards practical arsenic mitigation in complex water matrices.

In this study, humic acid sodium salt ($C_9H_8Na_2O_4$) was used to modify Fe_3O_4 MNPs to prevent aggregation and increase colloidal stability, thereby enhancing the As(V) adsorption performance of Fe_3O_4 . As(V) was selected due to its high stability and widespread occurrence in oxygenated aquatic environments, particularly in surface waters, where it primarily exists as oxyanions, whereas As(III) is more prevalent under reducing conditions and exhibits lower adsorption efficiency because its neutral molecular form at environmentally relevant pH limits interaction with adsorbent surfaces. The influence of key parameters, namely pH, Fe_3O_4 /HA MNP dosage, adsorption time, and the presence of coexisting ions, on As(V) removal was evaluated using the Taguchi method. The optimal conditions obtained from the Taguchi experiments were then used to investigate the adsorption kinetics of As(V). Furthermore, the crystallinity, morphology, elemental composition, and specific surface area of Fe_3O_4 and Fe_3O_4 /HA MNPs were characterized to better correlate material properties with adsorption performance.

2. Experimental

2.1 Chemicals and reagents

Sodium arsenate heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$, 98.0–102 %, Alfa; providing Na^+ and $HAsO_4^{2-}$), sodium sulfate (Na_2SO_4 , 99.14 %, Choneye Pure Chemicals; providing Na^+ and SO_4^{2-}), sodium nitrate $NaNO_3$, Shimakyu's Pure Chemicals; providing Na^+ and NO_3^-), calcium chloride anhydrous ($CaCl_2$, 76.07%, Choneye Pure Chemicals; providing Ca^{2+} and Cl^-), and trisodium phosphate (Na_3PO_4 , 97.9 %, Choneye Pure Chemicals; providing Na^+ and PO_4^{2-}) were obtained from their respective suppliers. Additional chemicals included ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99.9 %, Panreac AppliChem), ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, 99.5–104.5 %, Panreac AppliChem), humic acid sodium salt ($C_9H_8Na_2O_4$, 45–70 %, Acros), trisodium citrate dihydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$,

99–100.5 %, Panreac AppliChem), sodium hydroxide (NaOH, 98.0 %, Panreac AppliChem), ethanol (C₂H₅OH, 99.5 %, Shimakyu's Pure Chemicals), ammonia water (NH₄OH, 30%, Panreac AppliChem), nitric acid (HNO₃, 69 %, Panreac AppliChem), cadmium nitrate tetrahydrate (Cd(NO₃)₂·4H₂O, 99 %, Alfa), hydrochloric acid (HCl, 35–37 %, Shimakyu's Pure Chemicals), and potassium dichromate (K₂Cr₂O₇, Showa). High-purity nitrogen gas (N₂, 99.99 %, DaJun Gas) was used in all experimental procedures.

2.1. Preparation of Fe₃O₄ MNP and Fe₃O₄/HA MNP

The Fe₃O₄/HA MNP was synthesized via a co-precipitation method by using FeSO₄·7H₂O, FeCl₃·6H₂O and HA as the starting materials (**Figure 1**). First, FeCl₃·6H₂O and FeSO₄·xH₂O (molar ratio Fe³⁺:Fe²⁺ = 2:1) were dissolved in deionized (DI) water (100 mL) to form solution A. Separately, HA (0.5 g, 2 mmol) was dispersed in DI water (50 mL) under stirring to prepare solution B. Solution B was then gradually added to solution A under continuous stirring. The pH of the mixture was adjusted to pH 10 using ammonia solution, forming a black precipitate. The mixture was heated at 80°C under a nitrogen atmosphere with constant stirring for 30 min. The color of Fe₃O₄ MNP gradually changed from reddish-brown to black upon the formation of Fe₃O₄/HA MNP, indicating successful surface modification of the MNP with HA (**Figure S1**). After cooling to room temperature, the solid product was separated using a strong magnet and washed thoroughly with DI water and ethanol to remove impurities. The obtained Fe₃O₄/HA MNP composite was dried in a vacuum oven at 60°C, ground into fine powder, and stored for further use.



Figure 1. Schematic preparation of $\text{Fe}_3\text{O}_4/\text{HA}$ MNP via co-precipitation method

2.2. Design of experiment by Taguchi method

The solution pH, MNP dosage, adsorption time, and coexisting ions are the essential factors in the removal of heavy metals from aqueous solutions [24, 26, 27]. These factors could govern the binding of heavy metals to HA, therefore the adsorption capacity of Fe_3O_4 MNP [28]. For instance, the binding of heavy metals to the negatively charged surface of HA, which contains carboxylic and phenolic moieties, are strongly affected by solution pH and ionic charge [28, 29]. Therefore, it is important to assess these parameters when considering the application of $\text{Fe}_3\text{O}_4/\text{HA}$ MNP in removing As(V) in environment. In this work, Taguchi experiments were designed to determine the optimal operational conditions for the removal of As(V) [30, 31]. The four factors, which were solution pH, MNP dosage (g/L), adsorption time (min) and ionic concentration (mg/L) at four different levels, were evaluated in the Taguchi experiment and are shown in **Table 1**.

Table 1. Factors and levels used in the Taguchi experimental design

	Level 1	Level 2	Level 3	Level 4
Solution pH	3	5	7	9

Dosage of MNP (g/L)	1	3	5	7
Adsorption time (min)	30	80	130	180
Ionic concentration (mg/L)	20	40	60	80

At the beginning of the experiment, DI water (500 mL) was filled in the high-density polyethylene containers containing $\text{HAsNa}_2\text{O}_4 \cdot 7\text{H}_2\text{O}$ (98.0 %, 2 mg/L) and four kinds of coexisting ions, Na_2SO_4 (Na^+ , SO_4^{2-}), NaNO_3 (Na^+ , NO_3^-), CaCl_2 (Ca^{2+} , Cl^-), and Na_3PO_4 (Na^+ , PO_4^{3-}). These coexisting ions were chosen because they are among the most abundant ions in wastewater. The ionic concentrations were 20, 40, 60, and 80 mg/L. After adding these ions to the container, the solution pH was adjusted to 3, 5, 7, and 9 by using HNO_3 (0.1 M) and NaOH (0.1 M). The $\text{Fe}_3\text{O}_4/\text{HA}$ MNP was then added at the dosage of 1, 3, 5 and 7 g/L. A rotary oscillator (TKS, OS701) was deployed to shake the solutions. The adsorption time was initially set to 30, 80, 130, and 180 min to control the contact time between the magnetic adsorbent and arsenic in the solution. The As(V) concentration in the filtrates were measured using Atomic Absorption Spectroscopy (50 AA-AAS, Agilent Technologies).

2.3. Pseudo-second-order kinetic model

A pseudo-second-order kinetics model was employed to simulate the adsorption kinetics of As(V) by the $\text{Fe}_3\text{O}_4/\text{HA}$ MNP. Two $\text{Fe}_3\text{O}_4/\text{HA}$ MNP dosages (3 g/L and 5 g/L) were added into the As(V) solution (2 mg/L, 500 mL) at room temperature and pH 5. Kinetic experiments were carried out at pH 5, which represents a practically relevant compromise between the statistically optimal pH 3 identified by the Taguchi design and real-world operating constraints such as acid consumption and corrosion risk. The As(V) solution also contained Na_2SO_4 , NaNO_3 , CaCl_2 , and Na_3PO_4 , and the concentration of

each coexisting ion was 20 mg/L. The reaction time for the kinetic model was 180 min, and the adsorption capacity of Fe₃O₄/HA MNP was analyzed at 10, 20, 30, 40, 50, 60, 90, 120, and 180 min.

The amount of As(V) adsorbed at equilibrium (q_e , mg/g), the pseudo-second-order reaction, and the rate of the pseudo-second-order reaction (t/q_t) were calculated by using Eqs (1), (2) and (3), respectively [32].

$$q_e = \frac{(C_0 - C_e)}{m} V \quad (1)$$

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (2)$$

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

where C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of As(V), respectively; m (g) is the mass of Fe₃O₄/HA MNP, and V (L) is the volume of the As(V) solution, q_t is the amount of As(V) adsorbed at time t (min), k_2 is the reaction rate constant g/(mg·min). The feasibility of the pseudo-second-order kinetics model was evaluated based on the experimental results.

2.4. Characterization of adsorbents

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) (S-4800N, Hitachi) were used to analyze the surface characteristics and elements of synthesized materials. The crystal structure of Fe₃O₄ MNP and Fe₃O₄/HA MNP was determined by X-ray diffraction (XRD) D8 advance, Bruker, $\lambda = 1.542 \text{ \AA}$ with a Cu K α

radiation. The specific surface area of the samples was determined by the Brunauer Emmett Teller (BET) method.

3. Results and Discussion

3.1 Morphology of Fe₃O₄ MNP and Fe₃O₄/HA MNP

Composition and morphology of Fe₃O₄ MNP and Fe₃O₄/HA MNP are shown in **Figure 2**. The EDS results confirmed the presence of Fe and O in Fe₃O₄ MNP (**Figure 2(a)**), whilst Fe, O, and C elements were found in Fe₃O₄/HA MNP (**Figure 2(c)**). The C element was attributed to the addition of HA to Fe₃O₄ MNP. The weight percentages (%) of Fe and O in Fe₃O₄ MNP were 67.64 % and 32.36 %, respectively. The atomic ratio of Fe to O was close to 3: 4. As for Fe₃O₄/HA MNP, the weight percentage of Fe decreased with the addition of HA. The SEM images of the Fe₃O₄ MNP (**Figure 2(b)**) and Fe₃O₄/HA MNP (**Figure 2(d)**) reveal aggregation of unmodified Fe₃O₄ MNP, which was reduced substantially in Fe₃O₄/HA MNP, suggesting that HA helped in preventing the agglomeration whilst stabilizing of Fe₃O₄ MNP [33].

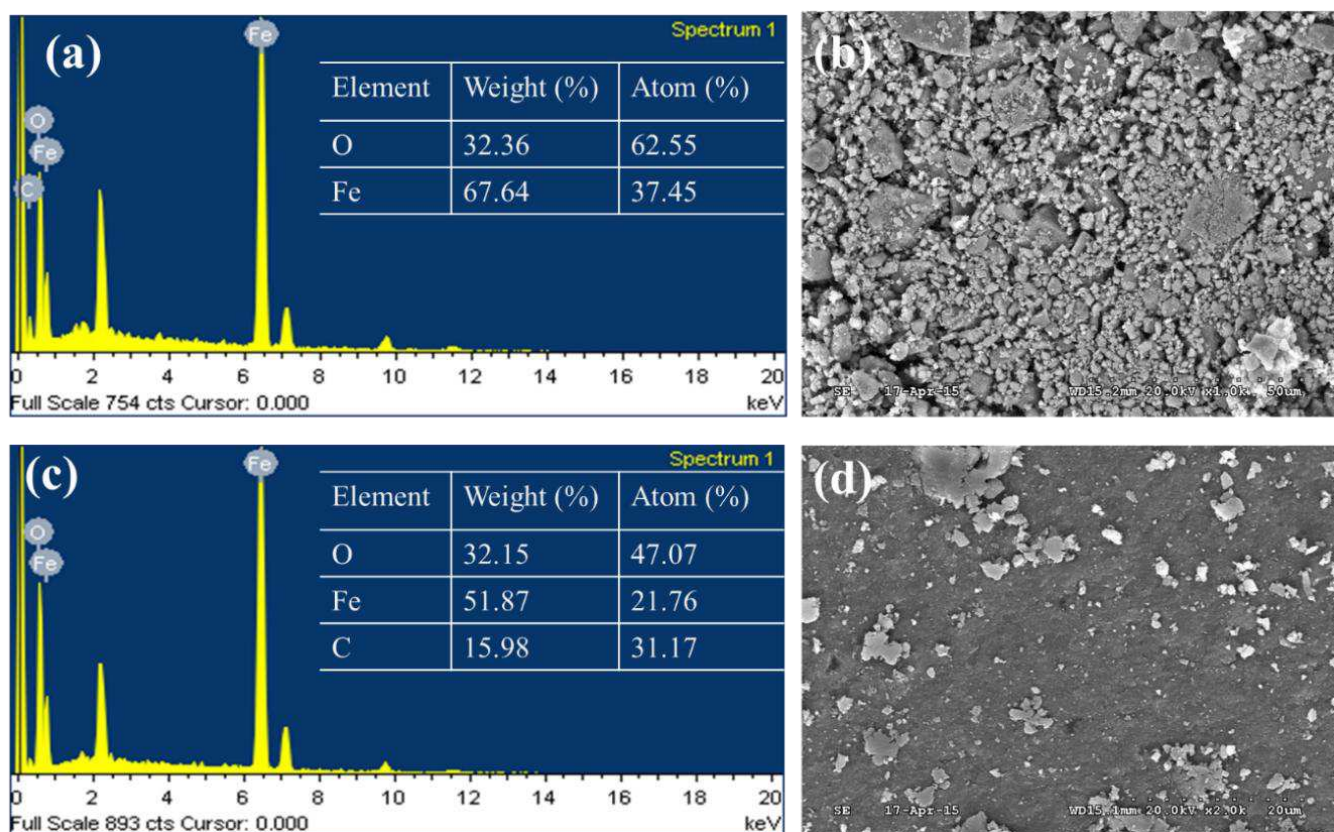


Figure 2. The EDS mapping and SEM images of (a, b) Fe₃O₄ MNP and (c, d) Fe₃O₄/HA MNP

3.2. Crystal structure and specific surface area of adsorbents

The XRD patterns of Fe₃O₄ MNP and Fe₃O₄/HA MNP are compared in **Figure 3**, and the characteristic peaks at 30.1°, 35.5°, 43.1°, 53.4°, 57.0°, and 62.6° corresponded to (220), (311), (400), (422), (511) and (440) planes of the Fe₃O₄ MNP, respectively. For the Fe₃O₄/HA MNP, there were no additional peaks and peak shifting, revealing that the crystallinity of MNP was not affected by the HA modification on the surface [33, 34].

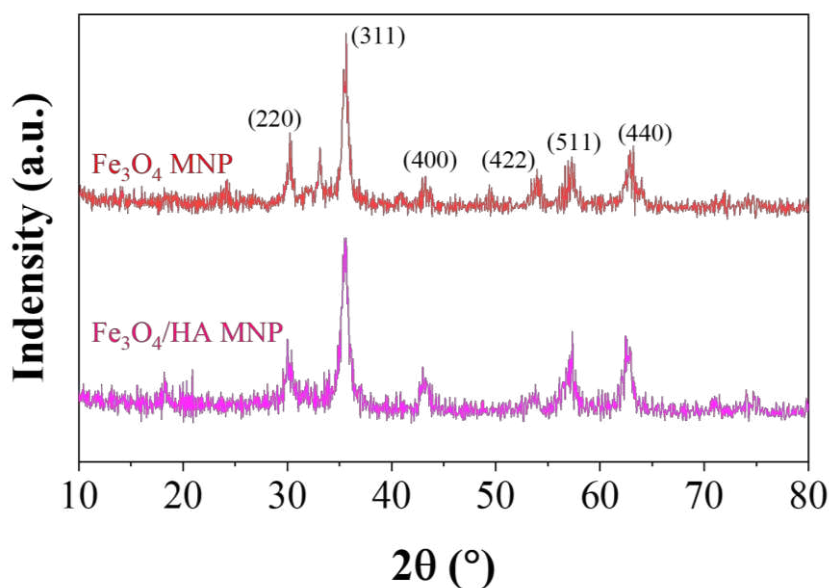


Figure 3. XRD patterns of Fe₃O₄ MNP and Fe₃O₄/ HA MNP

The specific surface area of the MNP adsorbents was calculated by the BET isotherm, as shown in **Figure S2**. The total specific surface area of Fe₃O₄/HA MNP (92.2 m²/g) was higher than that of Fe₃O₄ MNP (48.2 m²/g). The SEM micrographs (**Figure 2**) and BET isotherms (**Figure S2**) revealed efficiently reduced agglutination of Fe₃O₄/HA MNP [35, 36]. Furthermore, based on the XRD and BET results, the specific surface area of Fe₃O₄/HA MNP was greatly enhanced without affecting the crystallinity of Fe₃O₄ MNP [37], which are highly desired properties for Fe₃O₄-based adsorbents. The specific surface areas of Fe₃O₄ MNP and Fe₃O₄/HA MNP in this study are also compared with previous studies in **Table 2**. The specific surface area of our Fe₃O₄/HA MNP increased by 47.8 %, which was much higher than previously reported Fe₃O₄/HA MNPs (3.1 - 26.3 %), which were synthesized via hydrothermal and co-precipitation methods.

Table 2. Comparison of BET analyses of Fe₃O₄/HA MNP

Magnetic source	Modification	Modification method	Specific surface area (m ² /g)		Reference
			Before modification	After modification	
FeCl ₃ ·6H ₂ O, FeSO ₄ ·7H ₂ O	Humic Acid	Co-precipitation	48.2	92.2	This study
FeCl ₃ ·6H ₂ O, FeSO ₄ ·7H ₂ O	Humic Acid	Co-precipitation	89.5	102.8 - 121.4	[34]
FeCl ₃ ·6H ₂ O, FeCl ₂ ·4H ₂ O	Fluoropolymer , Humic Acid	Co-precipitation	15.4	24.5 - 29.8	[38]
FeCl ₃ ·6H ₂ O, FeCl ₂ ·4H ₂ O	Humic Acid	Co-precipitation	—	104	[39]
FeCl ₃ ·6H ₂ O, FeSO ₄ ·7H ₂ O	Humic Acid	Co-precipitation	62	64	[28]
FeCl ₃ ·6H ₂ O, FeSO ₄ ·7H ₂ O	Montmorillonite, Humic Acid	Hydrothermal	72.2	62.1 - 98.8	[40]
FeCl ₃ ·6H ₂ O, FeSO ₄ ·7H ₂ O	Oyster Shell, Humic Acid	Co-precipitation	-	47.5	[41]
FeCl ₃ ·6H ₂ O, FeSO ₄ ·7H ₂ O	Humic Acid	Co-precipitation	42.5	64	[42]

214 3.3. Optimization of As(V) removal by Taguchi method

215 The Taguchi method was used to optimize the operating conditions for adsorbing
 216 As(V) by using Fe₃O₄/HA MNP. The As(V) removal efficiency (y, %) and average

Signal-to-Noise ratio, (S/N, in unit dB) were calculated by Eqs (4) and (5), respectively [43].

$$\text{Removal efficiency, } y \text{ (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (4)$$

where C_0 (ppm) is the initial concentration of As(V), C_t is the concentration of As(V) at the time t (min) of the adsorption process.

$$\text{Signal - to - Noise ratio, } \frac{S}{N} = -10 \log\left(\frac{1}{n} \sum_{i=1}^n \frac{1}{y_i^2}\right) \quad (5)$$

The S/N is a robust evaluation index in the Taguchi experiments. The "larger the better" quality characteristic was selected in the experiment, in which the S/N ratio is equal to η , and y is the characteristic response or output. The experiments were conducted in triplicate under different experimental factors to determine the As(V) removal efficiency of Fe₃O₄/HA MNP, as shown in **Table S1**. Four experimental parameters were investigated in four levels, which were the solution pH (3, 5, 7, 9), the MNP dosage (1, 3, 5, 7 g/L), adsorption time (30, 80, 130, 180 min) and the coexisting ionic concentrations (20, 40, 60, 80 mg/L).

The highest As(V) removal efficiency and S/N value of Fe₃O₄/HA MNP were 94.3 % and 39.5 dB, respectively. The results show that Fe₃O₄/HA MNP reached the highest As(V) removal at pH 5, Fe₃O₄/HA MNP dosage of 5 g/L, adsorption time of 180 min, and ionic concentration of 20 mg/L. In addition, average S/N ratio of each factor was calculated for all four different levels, as shown in **Table S2**. The order of the S/N ratios among the four levels was pH value (0.25 dB) > MNP dosage (0.23 dB) > ionic

concentration (0.15 dB) > adsorption time (0.13). Overall, the solution pH was the most important factor in controlling the As(V) removal in aqueous solutions, whilst the adsorption time was the least critical factor in the As(V) removal.

Figure 4 depicts the S/N ratios of the residual tensile strength of the factors in this study. The dotted horizontal line in **Fig. 4** represents the overall mean S/N ratio across all experimental conditions, serving as a reference threshold for performance assessment, and S/N ratios exceeding this line indicate enhanced performance, whereas lower values suggest a decline in adsorption efficiency. The As(V) removal of Fe₃O₄/HA MNP decreased with increasing solution pH because of high redox potential of Fe₃O₄/HA MNP in low pH conditions. Lower redox potentials of Fe₃O₄/HA MNP at higher pH reduced the adsorption efficiency of Fe₃O₄/HA MNP [44], especially at pH ≥ 5, with the S/N ratio at 39.33. The highest S/N ratio of 39.38 was observed for the Fe₃O₄/HA MNP dosage of 5 g/L, before decreasing to 39.33 at the adsorbent dosage of 7 g/L, owing to the agglomeration tendency of Fe₃O₄/HA MNP at higher MNP dosages, leading to reduced the As(V) adsorption. For the adsorption duration, the highest S/N value (39.33) was recorded at adsorption duration of 80 min, before decreasing to 39.20 at 130 min and increased slightly to 39.25 at 180 min. As the S/N ratio of adsorption time was the lowest among other tested parameters, this confirms that the adsorption time is the least critical operational parameter in these Taguchi-optimized experiments.

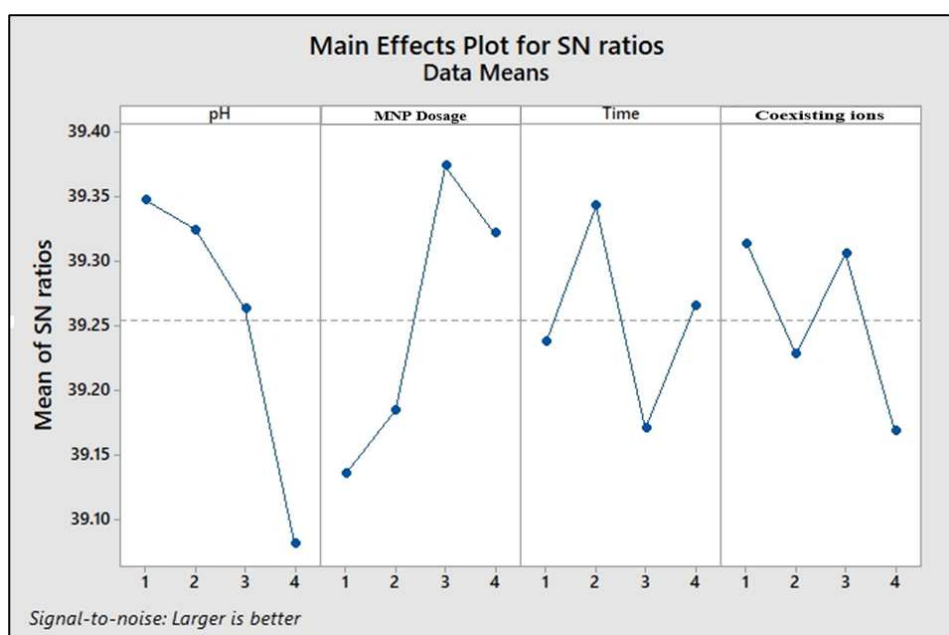


Figure 4. Mean data plots of S/N ratios at different experimental factors.

Coexisting ions (PO_4^{3-} , SO_4^{2-} , NO_3^- , Ca^{2+}) in the solution significantly influence the As(V) adsorption efficiency of $\text{Fe}_3\text{O}_4/\text{HA}$ MNP, as evidenced by a fluctuating S/N ratio trend. Herein, the S/N ratio of the coexisting ions reached the highest value at 39.33, with the concentration of the coexisting ions at 20 mg/L. In contrast, the S/N ratio of the coexisting ions decreased dramatically (39.18) at the ionic concentration of 80 mg/L, suggesting that higher ionic concentrations substantially hindered adsorption efficiency due to competitive interactions at the adsorption sites. While the experiments primarily focused on anions, due to their direct competition with As(V) as arsenate (AsO_4^{3-}), the role of cations (Na^+ and Ca^{2+}) must also be considered in the As(V) adsorption, as Na^+ in this study originated from Na_2SO_4 , NaNO_3 , and other related compounds. The specific inclusion of Ca^{2+} in the analysis is due to its ability to compress the diffuse double layer of $\text{Fe}_3\text{O}_4/\text{HA}$ MNP, altering the surface charge distribution and inducing particle aggregation [45]. Ca^{2+} interacts with carboxylate ($-\text{COO}^-$) and hydroxyl ($-\text{OH}$) moieties in HA, facilitating the formation of $\text{Fe}_3\text{O}_4/\text{HA}$ MNP complexes [46, 47]. Therefore, Ca^{2+} could promote adsorption efficiency by increasing the availability of active sites on the surface of $\text{Fe}_3\text{O}_4/\text{HA}$ MNP. However, at elevated concentrations of coexisting ions (80 mg/L), competitive adsorption effects become more pronounced, reducing the number of available adsorption sites and subsequently diminishing the adsorption efficiency [44]. Similarly, Na^+ influences As(V) adsorption through distinct mechanisms. As a monovalent cation, Na^+ has limited ability to compress the diffuse double layer. Instead, it primarily acts as a background electrolyte, increasing the ionic strength of the solution. At higher Na^+ concentrations, elevated ionic strength induces electrostatic screening, weakening the attraction between $\text{Fe}_3\text{O}_4/\text{HA}$ MNP and As(V), thereby reducing adsorption efficiency [45, 48, 49]. While Na^+ does not directly compete with As(V) for

the same adsorption sites due to their opposite charges, it can indirectly affect availability by binding to the negatively charged HA functional groups, slightly altering the surface charge [50, 51]. Compared to Ca^{2+} , Na^{+} has a weaker impact because it does not form stable inner-sphere complexes with HA functional groups, limiting its influence to predominantly electrostatic effects rather than chemical interactions. Notably, **Figure 4** indicates that the S/N ratio at level 3 (60 mg/L) was higher than at level 2, suggesting that ionic interactions and adsorption efficiency are not linearly dependent on concentration. This non-linear trend implies that complex ion-exchange dynamics may be occurring, warranting further investigation to fully elucidate their role in $\text{Fe}_3\text{O}_4/\text{HA}$ MNP adsorption performance. Therefore, the optimal As(V) removal conditions identified by the Taguchi method were: pH 3, $\text{Fe}_3\text{O}_4/\text{HA}$ MNP dosage of 5 g/L, contact time of 180 min, and coexisting ion concentration of 20 mg/L. At these conditions, anionic competition is minimized and cation effects are optimally balanced, enabling enhanced adsorption efficiency.

3.4. Adsorption Kinetics

Second-order kinetic models were used to assess the adsorption kinetics of As(V) by $\text{Fe}_3\text{O}_4/\text{HA}$ MNP utilizing the optimal conditions for the As(V) adsorption identified based on the Taguchi experimental results. Although the solution pH 3 exhibited the highest S/N ratio among all test levels, solution pH 5 (with an S/N ratio lower by 0.02 dB compared to pH 3) was selected for the reaction kinetics due to greater cost-effectiveness in practical applications.

Based on the results in **Fig. 4**, the As(V) adsorption kinetics of $\text{Fe}_3\text{O}_4/\text{HA}$ MNP with the MNP dosages of 3 g/L and 5 g/L at pH 5 were investigated and the results for the

heavy metal removal are shown in **Fig. 5**. The adsorption process was found to be rapid in the first 10 min of adsorption until reaching equilibrium at 180 min, with q_t being 0.404 and 0.44 for the 3g/L and 5g/L dosages, respectively. The initial fast adsorption rate of As(V) might be due to the nanoscale adsorbents since fine particles were favored for the diffusion of arsenic compounds from the bulk solution to the active sites of the adsorbents. Thus, the MNP showed high adsorption capacities at the beginning. The adsorbent's number of active sites reduced gradually with time, so As(V) adsorption gradually slowed down. The reaction kinetics constant (k_2), regression coefficient (R_2), equilibrium adsorption capacity (q_e), and the pseudo-second-order reaction rate (t/q_t) are shown in **Fig. 5(b)** and **Table S3**. The reaction kinetics constant (k_2) of the adsorbent dosage of 3 g/L was 0.156 g/(mg·min), which was lower than k_2 of the dosage of 5 g/L, which was 0.222 g/(mg·min).

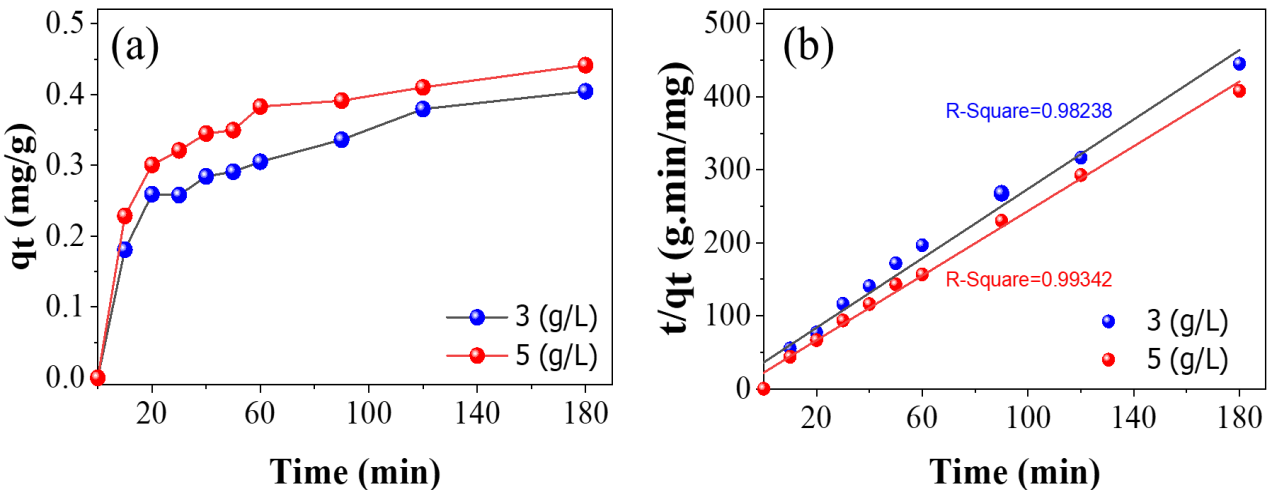


Figure 5. (a) As(V) adsorption kinetics of Fe₃O₄/HA MNP; and (b) the pseudo-second-order model for As(V) adsorption on Fe₃O₄/HA MNP

In contrast, t/q_t of the MNP dosage of 3 g/L was 445.2 g·min/mg, which was higher than the t/q_t of 5 g/L MNP dosage at 407.9 g·min/mg. In addition, q_e of As(V) at the MNP

dosage of 3 g/L and 5 g/L were 0.421 mg/g and 0.452 mg/g, respectively. These results show the adsorption capacity is directly proportional to the adsorbent dosage. However, the adsorption capacities did not differ much between 3 – 5 g/L adsorbent dosages, and the reaction kinetic constant of 5 g/L dosage was higher than that of 3 g/L. Comparing the q_e and k_2 values of our study with the literatures (**Table 3**), our q_e results were lower, however, the adsorption efficiencies of 3 g/L and 5 g/L achieved highest at 92.7 and 94.3 %, respectively (**Table S1**). The findings could be explained by low concentrations of As(V) with high adsorbent dosage. Moreover, the As(V) concentration used in this study (2 mg/L) is relatively low compared with many laboratory adsorption studies, and was selected to better reflect severely contaminated natural waters and industrial effluents, rather than treated drinking water where As levels are typically in the $\mu\text{g/L}$ range. The rate constant k_2 for 3 g/L MNP dosage (0.156 g/(mg·min)) was lower than that for 5 g/L (0.222 g/(mg·min)), indicating that higher adsorbent loadings promote faster As(V) adsorption kinetics, likely due to enhanced surface area and active site availability [52].

342

Table 3. Comparison of adsorption capacities with previous reports.

Adsorbent	Pollutant	Concentration (mg/L)	Contact time (min)	Dose (g/L)	q_e (mg/g)	k_2 g/mg·min	Ref.
Activated biochar covered with Fe_3O_4 nanoparticles (BCA-Fe)	As(V)	10	60	2	5	0.12	[53]
Fe_3O_4 -functionalized boron nitride nanosheets (BNNS- Fe_3O_4 nanocomposite)	As(III)	25	480	0.4	25.77	0.002	[54]
Iron-containing	As(V)	0.4	180	0.2	1.879	0.475	[55]

sludge (iMNP)							
Sol-gel derived Fe ₃ O ₄ quantum dot decorated silica composites	As(III)	10	90	0.15	38.2	0.043	[56]
TiO ₂ nanoparticles anchored on Fe ₃ O ₄ magnetic nanosheets	As(III); As(V)	0.91; 1.06	180	0.32	1.04; 3.35	0.212; 0.147	[57]
Polyaniline-Fe ₃ O ₄ - silver diethyldithio- carbamate nanostructures	As	0.045	N/A	N/A	138.88	0.0056	[58]
Fe ₃ O ₄ /Bentonite nanoparticles	As	20	120	5	6.8	0.001	[59]
Sulfur-doped Fe ₃ O ₄ nanoparticles	As(V)	20	1440	0.5	42.44	0.002	[60]
Fe ₃ O ₄ /HA MNPs	As(V)	2	180	5	0.452	0.222	This Study
Fe ₃ O ₄ /HA MNPs	As(V)	2	180	3	0.421	0.156	This Study

344

345 3.5 Adsorption mechanism

346 Heavy metal adsorption mechanisms are commonly classified into four main
347 categories: electrostatic interactions, ionic exchange, surface complexation/chelation, and
348 surface physical adsorption [47, 61]. In this context, the HA coating on Fe₃O₄/HA MNP
349 enriched the adsorbent's surface with carboxyl (C=O), phenolic hydroxyl (OH), and
350 carboxylate (COO⁻) functionalities, which play a crucial role in the complexation of As(V)
351 to the adsorbent [47, 62]. Based on the Taguchi analysis, the adsorption of As(V) onto
352 Fe₃O₄/HA MNP is primarily governed by the first three mechanisms, which are the
353 electrostatic interactions, ionic exchange, and surface complexation, supported by the
354 functional groups and the nanoscale structure of the MNP surface. At pH > pH_{pzc} (2.5),
355 the negatively charged surface of the material facilitates strong electrostatic interactions
356 with the As(V) ions, achieving an optimal adsorption efficiency of 94.3 % at pH 5. Ionic
357 exchange is evidenced by the replacement of surface-bound Ca²⁺ ions with As(V), while

high concentrations of coexisting ions (>20 mg/L) indicate competition for similar adsorption sites and gradually reduce the adsorbent's efficiency. The adsorption process follows the pseudo-second-order kinetics, with a rate constant (k_2) of 0.222 g/(mg·min) at a MNP dosage of 5 g/L. With a high surface area (92.2 m²/g) and structural stability, Fe₃O₄/HA MNP demonstrates strong potential as an efficient adsorbent for As(V) in wastewater treatment applications.

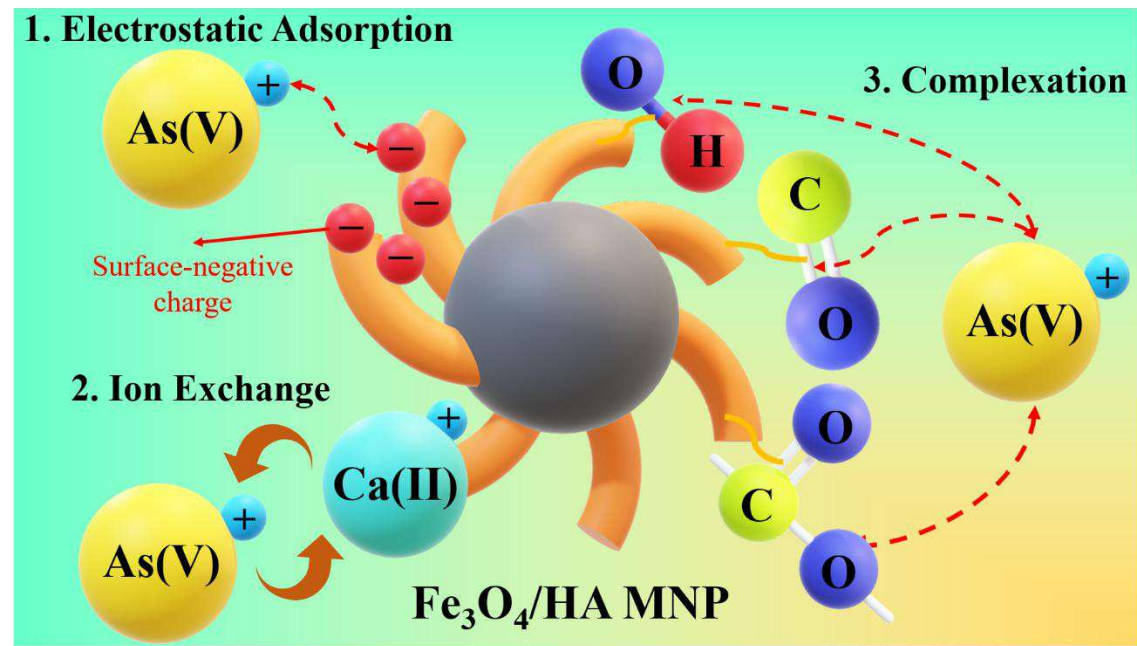


Figure 6. Proposed adsorption mechanism of As(V) on Fe₃O₄/HA MNP via electrostatic interaction, ionic exchange, and surface complexation.

4. Conclusions

The chemically modified Fe₃O₄/HA MNP showed high stability without aggregation compared to the unmodified Fe₃O₄ MNP. The Fe₃O₄/HA MNP also exhibited a larger specific surface area of 92.2 m²/g, much higher than the values (72.6 – 79.5 m²/g), which is favorable for enhancing arsenic adsorption performance. The Taguchi method

successfully identified the optimal operational conditions for As(V) removal using Fe₃O₄/HA MNP, namely pH 3, MNP dosage of 5 g/L, adsorption time of 180 min, and a coexisting ion concentration of 20 mg/L, under which the highest As(V) removal efficiency of 94.3% was achieved. The rapid removal of As(V) by Fe₃O₄/HA MNP was found to follow pseudo-second-order kinetics, involving electrostatic interactions, ion exchange, and surface complexation. The findings demonstrate the potential of Fe₃O₄/HA MNP as an effective and sustainable material for arsenic removal in wastewater treatment. Importantly, the optimization was conducted in the presence of multiple coexisting ions (PO₄³⁻, SO₄²⁻, NO₃⁻, Ca²⁺), providing practical insights into Fe₃O₄/HA MNP performance under realistic water-chemistry conditions. Future work should focus on evaluating performance at lower As levels (µg/L range), investigating adsorbent regeneration and reusability, and conducting column studies to translate these batch results into operational guidelines for field-scale applications.

388 **Declarations**

389 **Ethics Approval**

390 Not applicable.

391 **Consent for Participation and Publication**

392 Not applicable.

393 **Availability of data and materials**

394 No datasets were generated or analyzed during the current study. Data sharing is not
395 applicable to this article.

396 **Competing interests**

397 The authors declare that they have no competing financial or non-financial interests
398 related to the work described in this manuscript. None of the authors is registered in the
399 journal's Editorial System as an Editor or Reviewer, and none of the authors is a member
400 of the Editorial Board of *Chemical Papers*.

401 **Clinical Trial Registration**

402 Not applicable.

403

404 **References**

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