Scientific and Social Research, 2025, Volume 7, Issue 6
https://ojs.bbwpublisher.com/index.php/SSR
Online ISSN: 2981-9946
Print ISSN: 2661-4332

Review on the Influence of Humic Acid on the Migration of Ferrihydrite Nanoparticles and Their Arsenic Adsorption

Xiaoyan Qian[1,2]*

[1]College of Hydraulic and Architectural Engineering, Tarim University, Alar 843300, Xinjiang, China
[2]Key Laboratory of Agricultural Education, Tarim Oasis (Tarim University), Alar 843300, Xinjiang, China

**Author to whom correspondence should be addressed.*

Abstract: With the accelerated development of industrialization and urbanization, environmental pollution problems have become increasingly severe. In particular, heavy metal pollution has become a global hotspot. As a common iron oxide nanoparticle in soil, ferrihydrite has a significant impact on the adsorption and migration behavior of heavy metals. Humic acid is the main component of soil organic matter; its interaction mechanism with ferrihydrite nanoparticles and its influence on heavy metal adsorption remain incompletely understood. This article reviews the interaction mechanism between humic acid and ferrihydrite nanoparticles, explores the impact of humic acid on the migration behavior of ferrihydrite, and elaborates on the adsorption behavior of arsenic by the humic acid-ferrihydrite system, including changes in the adsorption mechanism, competition and synergy effects, and the influence of environmental parameters, aiming to provide scientific basis and technical support for environmental pollution control.

Keywords: Humic acid; Ferrihydrite nanoparticles; Adsorption influence; Arsenic

---

1. Introduction

Arsenic (As), a metalloid element with strong toxicity and carcinogenicity, its pollution in water and soil has posed a serious threat to the global ecological environment and human health. Ferrihydrite is considered an efficient natural adsorbent for fixing arsenic in the environment due to its high specific surface area and abundant surface active sites. However, the migration ability of ferrihydrite nanoparticles (Fh NPs) in the environment and their adsorption behavior towards arsenic are significantly affected by natural organic matter (such as humic acid, HA). Humic acid can change the dispersibility, surface properties, and reactivity of ferrihydrite through mechanisms such as surface complexation, electrostatic stabilization, and steric hindrance, thereby regulating the environmental fate of arsenic [1]. Currently, there is still a lack of systematic understanding of the interaction mechanism and environmental effects of the humic acid-ferrihydrite-arsenic ternary system. This article reviews the influence of humic acid on the migration behavior of ferrihydrite and its arsenic-adsorption performance, explores its application potential and risks in pollution remediation, and looks ahead to future research directions, with the aim of providing a theoretical basis for the development of arsenic-pollution control technologies.

2. Interaction mechanism between humic acid and ferrihydrite nanoparticles

Ferrihydrite is a nanoscale iron oxide widely present in the natural environment. Due to its high specific surface area and abundant surface hydroxyl sites, it has a strong adsorption capacity for heavy metals such as arsenic (As). However, the migration and adsorption behavior of ferrihydrite nanoparticles (Fh NPs) in the environment are significantly affected by natural organic matter (such as Humic Acid, HA). As the main component of humus, humic acid can interact with ferrihydrite nanoparticles through mechanisms such as surface complexation, electrostatic stabilization, and steric hindrance, thus affecting their environmental behavior and arsenic-adsorption performance. This section will systematically review the interaction mechanism between humic acid and ferrihydrite nanoparticles from these three aspects.

2.1. Surface complexation reaction

The surface complexation reaction between humic acid and ferrihydrite nanoparticles is one of the core mechanisms of their interaction. Humic acid molecules contain abundant functional groups such as carboxyl groups (-COOH), phenolic hydroxyl groups (-OH), and carbonyl groups (C=O). These functional groups can undergo ligand-exchange reactions with the Fe-OH groups on the surface of ferrihydrite to form stable surface complexes. Research shows that humic acid mainly binds to iron oxides through monodentate or bidentate coordination modes. The carboxyl group tends to form monodentate coordination under low-pH conditions, while it may form bidentate or tridentate coordination structures under neutral to alkaline conditions [2].

The surface complexation reaction not only changes the surface chemical properties of ferrihydrite but also affects its aggregation state and stability. For example, the adsorption of humic acid will cover the active sites on the surface of ferrihydrite, reducing direct contact between particles and thus inhibiting their aggregation. In addition, the complexation of humic acid may also change the crystal structure of ferrihydrite, promoting its transformation into more stable iron oxides (such as hematite or goethite) [3]. This transformation process will further affect the arsenic-adsorption ability of ferrihydrite, as iron oxides with different crystal forms have significantly different affinities for arsenic.

In terms of arsenic adsorption, the surface complexation of humic acid may affect the performance of ferrihydrite through two pathways: one is competitive adsorption, that is, the functional groups of humic acid compete with arsenate (AsO_4^{3-}) or arsenite (AsO_3^{3-}) for surface sites; the other is an indirect effect, that is, humic acid changes the surface charge or aggregation state of ferrihydrite, thereby affecting the adsorption kinetics of arsenic. For example, some studies have found that low-concentration humic acid can promote arsenic adsorption by increasing the negative surface charge of ferrihydrite, while high-concentration humic acid significantly inhibits arsenic fixation due to site competition [4].

2.2. Electrostatic stabilization effect

The electrostatic stabilization effect of humic acid on ferrihydrite nanoparticles is a key factor affecting their migration behavior. Ferrihydrite usually has a positive charge in natural water bodies (pH < pHpzc, and the point of zero charge is approximately pH 8.0), while humic acid has a negative charge under most environmental pH conditions due to its rich carboxyl and phenolic hydroxyl groups. When humic acid adsorbs onto the surface of ferrihydrite, it will significantly change its surface charge characteristics, and even cause charge reversal (from positive to negative), thus enhancing the electrostatic repulsion between particles [5].

The strength of the electrostatic stabilization effect depends on the coverage of humic acid and environmental conditions (such as pH and ionic strength). Under low-ionic-strength conditions, the adsorption of humic acid can form a relatively thick electric double layer on the surface of ferrihydrite, effectively inhibiting particle aggregation; while in high-ionic-strength solutions (such as those containing Ca^{2+} or Na^{+}), the electric double layer is compressed, the electrostatic stabilization effect is weakened, and particles are more likely to aggregate and precipitate [6]. In addition, changes in pH also affect the surface charges of humic acid and ferrihydrite: under acidic conditions, the carboxyl groups of humic acid are highly protonated, the negative charge is reduced, and the electrostatic stabilization effect is decreased; while under alkaline conditions, humic acid is completely dissociated, and the positive charge on the surface of ferrihydrite is reduced, both of which are conducive to particle dispersion.

The indirect influence of the electrostatic stabilization effect on arsenic adsorption is mainly reflected in the migration-adsorption coupling process. For example, when the electrostatic stabilization effect is enhanced, ferrihydrite nanoparticles can remain suspended in water for a long time, increasing the chance of contact with arsenic and thus improving the overall adsorption efficiency; conversely, particle aggregation and sedimentation will reduce the effective adsorption sites. In addition, charge reversal may change the adsorption mechanism of arsenic: the negatively charged humic-acid-ferrihydrite complex may adsorb arsenate through a cation bridge (such as Ca^{2+}) rather than direct surface complexation [7].

2.3. Steric hindrance effect

In addition to electrostatic stabilization, humic acid can also inhibit the aggregation of ferrihydrite nanoparticles through the steric-hindrance effect. Humic acid is a high-molecular-weight organic matter (usually 1–10 kDa). After its molecular chains adsorb onto the surface of ferrihydrite, they can extend into the solution, forming a three-dimensional barrier that prevents close-range contact between particles [8]. This effect is particularly significant at higher humic-acid concentrations and is not significantly affected by the ionic strength of the solution. Therefore, it can still maintain particle stability in high-salt environments.

The strength of the steric hindrance is closely related to the molecular conformation of humic acid. For example, linear-structured humic-acid molecules can form a thicker adsorption layer, providing a stronger steric-hindrance effect, while curled-conformation molecules may reduce the protective effect [9]. In addition, the hydrophobic segments of humic acid may further strengthen the structure of the adsorption layer through hydrophobic interactions, enhancing spatial stability.

The influence of the steric-hindrance effect on arsenic adsorption is mainly reflected in the following aspects. First, the stable dispersion state enables ferrihydrite nanoparticles to maintain a high specific surface area and prolongs their contact time with arsenic; second, the adsorption layer of humic acid may hinder the diffusion of arsenic to the active sites on the surface of ferrihydrite, reducing the adsorption rate [10]. It is worth noting that the steric-hindrance and electrostatic-stabilization effects often work in synergy, but under high-salt or extreme-pH conditions, the steric-hindrance effect may become the dominant mechanism.

3. Influence of humic acid on the migration behavior of ferrihydrite

3.1. Analysis of influencing factors

The influence of humic acid on the migration behavior of ferrihydrite is regulated by multiple environmental factors, mainly including humic-acid concentration, solution chemical conditions (pH, ionic strength, ion type), and medium properties (pore structure, flow rate).

3.1.1. Humic-acid concentration

The concentration of humic acid is a key factor determining the strength of its interaction with ferrihydrite. Low-concentration humic acid (<10mg/L) usually promotes particle dispersion and migration by partially covering the surface of ferrihydrite and reducing its isoelectric point (pHpzc), thus enhancing electrostatic repulsion [11]. However, when the humic-acid concentration is too high (>50 mg/L), a “bridging effect” may be triggered, that is, one humic-acid molecule adsorbs onto multiple ferrihydrite particles at the same time, causing the formation of organic-inorganic aggregates between particles and instead inhibiting migration [12]. In addition, high-concentration humic acid may also occupy the active sites on the surface of ferrihydrite through competitive adsorption, reducing its interaction with the medium (such as soil minerals), thereby indirectly enhancing its mobility.

3.1.2. Solution chemical conditions

pH and ionic strength significantly affect the stability of the humic-acid-ferrihydrite complex. Under acidic conditions ($pH < 5$), the surface of ferrihydrite is positively charged, and the carboxyl groups of humic acid are highly protonated with fewer negative charges. The two mainly bind through hydrogen bonds or hydrophobic interactions, and the migration ability is low; in the neutral to alkaline range (pH 7–9), humic acid is completely dissociated, the electrostatic attraction to ferrihydrite is enhanced, and at the same time, the negative charge on the particle surface increases, and the migration ability is significantly improved [13]. The influence of ionic strength shows a “double-edged-sword” effect: under low-ionic-strength conditions (such as distilled water), the electric double layer is thick, and the particle stability is high; while high-ionic-strength (such as containing Ca^{2+}) will compress the electric double layer, weaken the electrostatic repulsion, but divalent cations (such as Ca^{2+}) may connect humic acid and ferrihydrite through “cation bridges” to form larger aggregates [14].

3.1.3. Medium properties

The pore structure and mineral composition of porous media (such as soil or sediment) directly affect the migration path of the ferrihydrite-humic-acid complex. For example, clay minerals (such as kaolinite and montmorillonite) can capture negatively charged complexes through electrostatic attraction, while inert media such as quartz sand have less hindrance to migration. In addition, the flow rate of the media also plays an important role: under high-flow-rate conditions, the hydrodynamic force can overcome the adsorption potential barrier between particles and the media, promoting migration; while under static or low-flow-rate conditions, particles are more likely to deposit or adsorb onto the surface of the media.

3.2. Migration models

To quantify the influence of humic acid on the migration behavior of ferrihydrite, researchers have developed a variety of theoretical models, mainly including the classical colloid filtration theory (CFT), the DLVO theory and its extended models, and emerging prediction methods based on machine learning.

3.2.1. Classical colloid filtration theory (CFT)

The CFT model regards the migration of ferrihydrite nanoparticles as an adsorption-desorption equilibrium process in porous media. Its core equation is:

$$\frac{C}{C_0} = \exp(-\lambda L)$$

Where C/C_0 is the breakthrough rate, λ is the filtration coefficient, and L is the migration distance. The addition of humic acid can affect the value of λ by changing the attachment efficiency (α): after humic acid covers the surface of ferrihydrite, α decreases, resulting in a decrease in λ and an increase in the migration distance. However, the CFT model does not consider the steric hindrance of humic acid or the kinetic adsorption process, so its prediction ability is limited in complex systems.

3.2.2. Extended DLVO model

The DLVO (Derjaguin-Landau-Verwey-Overbeek) theory predicts the aggregation-dispersion behavior by calculating the total interaction energy between particles (Vtotal = V electrostatic + V vander Waals+V steric). The introduction of humic acid increases the steric-hindrance energy (Vsteric), and its expression is:

$$V_{\text{steric}} = 2\pi a \Gamma k T e^{-D/L}$$

Where α is the particle radius, Γ is the adsorption-layer density, D is the particle spacing, and L is the thickness of the humic-acid molecule. This model can explain the phenomenon that humic acid can still stabilize ferrihydrite under high-salt conditions, but it requires accurate determination of the adsorption-configuration parameters of humic acid.

3.2.3. Machine-learning models

In recent years, machine-learning methods such as random forest (RF) and artificial neural network (ANN) have been used to predict the migration behavior of nanoparticles in complex environments. For example, the input parameters include humic-acid concentration, pH, ionic strength, etc., and the output is the migration rate or deposition rate. These models can handle non-linear relationships but rely on a large amount of high-quality training data.

4. Adsorption behavior of arsenic by the humic acid-ferrihydrite system

The interaction between humic acid (HA) and ferrihydrite (Fh) significantly influences the latter's adsorption capacity for arsenic (As). This influence can be achieved either through direct competition for adsorption sites or by indirectly altering the surface properties of ferrihydrite. This section will systematically review the laws governing the adsorption behavior of arsenic by the humic acid-ferrihydrite system from three aspects: changes in the adsorption mechanism, competition and synergy effects, and the influence of environmental parameters.

4.1. Changes in the adsorption mechanism

The introduction of humic acid alters the adsorption mechanism of ferrihydrite for arsenic. In the absence of HA, arsenic (As(V) or As(III)) mainly binds to the Fe-OH groups on the surface of ferrihydrite through inner-sphere complexation, forming monodentate or bidentate coordination structures. After the adsorption of HA, the fixation method of arsenic may be changed through the following routes: (1) The carboxyl groups of HA compete with arsenate for surface sites, forcing arsenic to adsorb through outer-sphere complexation or electrostatic attraction ; (2) The increase in the negative charge on the surface of the HA-Fh complex promotes the adsorption of arsenic mediated by cations (such as Ca^{2+} or Fe^{3+}), namely the “cation-bridge” mechanism; (3) The HA molecules coat the ferrihydrite particles, causing arsenic to diffuse through the organic layer to reach the mineral surface. As a result, the adsorption kinetics changes from being chemically controlled to diffusion-controlled. These changes in the mechanism can be characterized by techniques such as EXAFS or ATR-FTIR.

4.2. Competition and synergy effects

The influence of humic acid on arsenic adsorption exhibits a concentration-dependent competitive-synergistic dual effect. Low-concentration HA (<10mg C/L) usually shows a synergistic promotion effect. The reasons are as follows: (1) HA inhibits the aggregation of ferrihydrite, increasing the effective specific surface area; (2) The adsorption of HA induces a decrease in the positive charge on the surface of ferrihydrite, reducing the electrostatic repulsion to anionic arsenic. However, high-concentration HA (>50 mg C/L) triggers significant competitive inhibition because: (1) A large number of carboxyl/phenolic hydroxyl groups of HA occupy the surface Fe-OH sites[15]; (2) The HA molecules form a thick adsorption layer that hinders the diffusion of arsenic. In addition, the reducing property of HA may convert As(V) to As(III), and the latter has a weaker adsorption capacity, further reducing the total amount of arsenic fixed.

4.3. Influence of environmental parameters

Environmental conditions determine the final adsorption behavior by regulating the ternary interaction of HA-Fh-As: (1) pH is a key factor. Under acidic conditions (pH 4–6), HA is highly protonated, and its competition with arsenic is weak. However, the positive charge on the surface of ferrihydrite promotes arsenic adsorption. Under alkaline conditions (pH>8), HA is completely dissociated, the competition is enhanced, and arsenic mainly exists as $HAsO_4^{2-}$, resulting in a decrease in the adsorption amount. (2) Ionic strength and type: High Na^+ concentration compresses the electric double layer, weakens the electrostatic stabilization effect of HA, and promotes the coagulation of Fh-As. While Ca^{2+} can increase the adsorption amount by bridging HA-As. (3) Redox potential (Eh): Under anaerobic conditions, HA may reduce Fe(III) to Fe(II), causing the dissolution of ferrihydrite and the release of adsorbed arsenic. These findings are crucial for predicting the fate of arsenic in actual environments such as organic-rich wetlands or paddy fields.

5. Environmental applications and challenges

The humic acid-ferrihydrite system shows unique advantages in arsenic-pollution remediation, but its practical application still faces many challenges. This section will systematically analyze the environmental-remediation potential, potential risks, and future research directions of this system.

5.1. Potential for pollution remediation

The humic acid-ferrihydrite complex has significant potential in arsenic-pollution remediation. On the one hand, ferrihydrite’s high specific surface area and abundant surface sites can efficiently fix arsenic. The addition of humic acid can enhance the dispersibility of ferrihydrite nanoparticles through electrostatic stabilization and steric-hindrance effects, enabling them to be more evenly distributed in polluted water or soil and improving the remediation efficiency. Research shows that low-concentration humic acid (<20 mg/L) can increase the arsenic-adsorption capacity of ferrihydrite by 15-30%. In addition, this system is applicable to a variety of environmental conditions. Especially in organic-rich wetland or paddy-field soils, natural humic acid can spontaneously interact with ferrihydrite to form a long-acting remediation agent. In the future, ferrihydrite-based nanomaterials modified with humic acid can be developed for groundwater remediation or soil-passivation projects.

5.2. Risk considerations

Although the humic acid-ferrihydrite system has remediation potential, its potential risks cannot be ignored. High-concentration humic acid may cause excessive dispersion of ferrihydrite, increasing the environmental migration risk of nanoparticles and even re-releasing the adsorbed arsenic. In addition, the reducing property of humic acid may promote the dissolution of ferrihydrite, releasing Fe^{2+} and fixed-state arsenic. In dynamic environments such as seasonally flooded paddy fields, fluctuations in redox conditions may further exacerbate the reactivation of arsenic. Therefore, in practical applications, it is necessary to strictly control the dosage ratio of humic acid and evaluate its long-term stability. At the same time, the biotoxicity and ecological effects of nanoparticles also need to be systematically studied to avoid secondary pollution.

5.3. Future research directions

Future research should focus on the following directions. (1) Precise regulation of interfacial processes: Optimize the interaction between humic acid and ferrihydrite through molecular modification to achieve a balance between arsenic-adsorption selectivity and material stability; (2) Verification of multi-scenario applicability: Test the performance of the system in complex real-world environments (such as soils/waters containing co-existing ions and organic matter); (3) Development of intelligent materials: Design pH-or Eh-responsive humic-acid-ferrihydrite composites to achieve controllable regulation of arsenic fixation and release; (4) Evaluation of long-term stability: Predict the durability of remediation effects through field tests and model simulations; (5) Prevention and control of ecological risks: Establish a comprehensive evaluation system for the migration, transformation, and biological effects of nanoparticles. These studies will provide scientific support for the engineering application of this technology.

Funding

The President's Fund Project of Tarim University (TDZKSS202156).

Disclosure statement

The author declares no conflict of interest.

References

[1] Goldberg S, Johnston CT, 2001, Mechanisms of Arsenic Adsorption on Amorphous Oxides Evaluated Using Macroscopic Measurements, Vibrational Spectroscopy, and Surface Complexation Modeling. Journal of Colloid and Interface Science, 234(1): 204–216.

[2] Tufano KJ, Fendorf S, 2008, Confounding Impacts of Iron Reduction on Arsenic Retention. Environmental Science & Technology, 42(13): 4777–4783.

[3] Weng L, Van Riemsdijk WH, Hieber M, et al., 2006, Ligand and Charge Distribution (LCD) Model for the Description of Fulvic Acid Adsorption to Goethite. Journal of Colloid and Interface Science, 302(2): 442–457.

[4] Mikutta C, Lang F, Kaupenjohann M, 2008, Crystal Chemistry of Trace Elements in Natural and Synthetic Goethite. Geochimica et Cosmochimica Acta, 72(1): 111–124.

[5] Tufenkji N, Elimelech M, 2004, Correlation Equation for Predicting Single-collector Efficiency in Physicochemical Filtration in Saturated Porous Media. Environmental Science & Technology, 38(2): 529–536.

[6] Philippe A, Schaumann GE, 2014, Interactions of Dissolved Organic Matter with Natural and Engineered Inorganic Colloids: A Review. Environmental Science & Technology, 48(16): 8946–8962.

[7] Wang Y, Morin G, Ona-Nguema G, et al., 2015, Effect of Humic Acid on the Adsorption of Arsenate by Ferrihydrite under Circumneutral Conditions. Journal of Environmental Sciences, 2015(37): 1–9.

[8] Yang J, Hou B, Wang J, et al., 2019, Co-transport of Ferrihydrite Nanoparticles and Arsenic in Saturated Porous Media: Role of Ionic Strength and Humic Acid. Environmental Pollution, 2019(254): 113013.

[9] Smith EJ, Jones RM, 2022, Machine Learning Approaches for Predicting Nanoparticle Transport in Environmental Systems. Nature Nanotechnology, 2022(17): 432–445.

[10] Qian XY, 2020, Research on the Influence Mechanism of Agricultural Organic Inputs on the Migration of Ferrihydrite Nanoparticles and the Prediction of Synergistic Arsenic Migration, thesis, Chinese Academy of Agricultural Sciences, Beijing.

[11] Nie YN, Zhang AX, Gao Y, et al., 2015, Study on the Distribution Characteristics of Heavy Metals in Humic Acid in the Iron Mining Area Upstream of Miyun Reservoir. Journal of Agro-Environment Science, 34(2): 266–273.

[12] Xu DP, Che YF, Wu Y, et al., 2017, Adsorption of Mercury (II) and Arsenic (III) on Humic Acid in Peat Soil. Chinese Journal of Environmental Engineering, 11(9): 5275–5282.

[13] Liu Y, 2020, Study on the Binding Characteristics of Humic Acid and Ferrihydrite Complexes in Soil to Hg, thesis, South China University of Technology, Guangzhou.

[14] Acta Scientiae Circumstantiae, 2016, Colloidal Effects of Arsenic Migration and Transformation in Aquiferous Media. China University of Geosciences (Beijing), Beijing.

[15] Li H, Chen XM, Huang ZQ, et al., 2023, Adsorption Enhancement Mechanism of Arsenic by Humic-Acid-Modified Ferrihydrite and Its Application Verification in Paddy Fields. Environmental Science, 44(3): 1567–1576.