



Article Ferrous Magnetic Nanoparticles for Arsenic Removal from Groundwater

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Abstract: Arsenic in water is currently a global concern due to the long-term exposure that could affect human health. In this study, magnetic nanoparticles (MNPs), $CoFe_2O_4$, and $MnFe_2O_4$ were successfully synthesized and applied to remove arsenic (As) from water. The MNPs were characterized using different techniques, such as scanning electron microscope (SEM), Brunauer–Emmet–Teller (BET), and photoelectron spectroscopy (XPS). The nanoscale size and the specific surface area achieved a fast, selective, and high As adsorption capacity. MNPs have a mesoporous structure with a mean pore diameter of 5 nm and a mean particle size of 30 nm. The adsorption capacity of these MNPs was determined through kinetic and equilibrium experiments, multilayer adsorption that obeyed the Freundlich model equation was observed, and the maximum adsorption capacities reached were 250 mg/g for CoFe₂O₄ and 230 mg/g for MnFe₂O₄. Furthermore, MNPs characteristics like regeneration and reuse, several pH tolerances, non-ion interference, and effective As removal from groundwater samples confirms the nanomaterials' potential for future applications in water treatment systems combined with magnetic separation.

Keywords: selective adsorption rate; maximum adsorption capacities; external magnetic field; arsenite removal; water purification systems

1. Introduction

Arsenic (As) pollution in water (groundwater) is one of the most critical environmental issues worldwide. Their most common species in aqueous environments are arsenite (As (III)), arsenate (As(V)), and elemental arsenic (As₀). Among these species, the As (III) compounds are more harmful than those constituted by As (V) [1]. Around the world, serious health effects have been observed in populations exposed to polluted water with As for an extended period. Permanent intake could cause the appearance of hyperkeratosis and arsenicosis (chronic endemic regional hydroarsenism, HACRE) [2]. Therefore, the World Health Organization (WHO) and the United States Protection Agency (EPA) approved 10 μ g/L, in the case of drinking water, as the As permissive limit, in order to avoid health effects [3].

According to the literature, different countries have reported arsenic in water in concentrations above the recommended limits, such as the United States, China, Chile, Bangladesh, Taiwan, México, Argentina, Poland, Canada, Hungary, and New Zealand [4].



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). In Latin America, the As presence in groundwater by geogenic origin is the main As source, and severe health problems due to water consumption with a high As content has been reported [2]. In Mexico, most of the population is exposed to a high As concentration in water; although As is classified as a carcinogenic contaminant of Group I [5], the Official Mexican Standard allows 25 μ g/L (NOM-127-SSA1-1994). Therefore, it is important to improve or develop suitable methodologies for As removal in drinking water to values under innocuous limits.

Several technologies have been developed for the treatment and removal of heavy metals in water [1,6]. Traditional treatment processes include coprecipitation [7], ion exchange [8], membrane separation [9], filtration/ultrafiltration [10], electrocoagulation [11], reverse osmosis [12], dialysis/electrodialysis [13], etc. Some of these processes highlight advantages such as chemical precipitation results in very efficient metal removal. The chemical precipitation method is simple to operate and does not require expensive equipment [14]. Ion exchange, electrodialysis, and electrochemistry have the ability to selectively remove the pollutant eVen simultaneously with organic pollutants. However, each process has some inherent disadvantages. For example, chemical precipitation generates a large amount of by-product in the form of sludge, resulting in a secondary pollutant. Ion exchange, the electrochemical process, membrane filtration, and electrodialysis have high operating and maintenance costs.

Adsorption is a promising method as it represents an easy-to-use, low-cost, and lowby-product-generation technique. Furthermore, it has been developed using synthetic and mineral removal materials [15–17]. Adsorption technology is a recognized method for removing heavy metals from water. Especially in developing countries where financial resources are an issue, this technique provides an easy way to remove heavy metals such as arsenic from water. Currently, magnetic hydroxyapatite nanocomposites, magnetic magnetite nanoparticles for Cr (VI) and Cu (II) coexisting in mixed solutions, and magnetic nanoparticles synthesized by greenways, etc., have been studied [18–20]. However, the adsorption efficiency depends on the type of adsorbents. This study aimed to determine the removal capacity of arsenite ions from natural water by magnetic nanoparticles (CoFe₂O₄ and MnFe₂O₄). The performance of these MNPs was eValuated under numerous conditions, such as the stability of the MNPs at different pH values, the contact time in the aqueous solution, the adsorbent dose, and the initial concentration of As (III), which could affect the adsorption process.

2. Materials and Methods

2.1. Nanoparticles Synthesis

All the precursors used in the experiments (analytical reactive grade) were used without further purification. The MNPs were prepared by the chemical coprecipitation method [21]. For the synthesis of the MnFe₂O₄ MNPs, Fe (NO₃)₃•9H₂O (Sigma Aldrich-Química, S.L Toluca, México), and MnSO₄•H₂O (Fermont-Productos químicos Monterrey S.A. de C.V. Monterrey, N.L.México J.T. Baker), precursors were dissolved in 5 mL of deionized water and HCl (1 mL, 1 M, Fermont), with a stoichiometry ratio of 2:1. First, the solution was mixed and vigorously stirred. Then, 100 mL of NaOH (Fermont) was added dropwise to 3 M. Once the addition was complete, it was brought to 90 °C for 60 min. The same procedure was applied for CoFe₂O₄ MNPs using CoSO₄•7H₂O (J.T. Baker Avantor Performance Materials, Inc., Center Valley, PA, USA). Next, the MNPs were recovered from the solution with a magnet and repeatedly rinsed with distilled water until neutral pH. Afterward, the values of pH were adjusted to 6, 7, 8, and 8.5. Finally, the products were taken to the oven at 100 °C for 24 h to subsequently grind them.

2.2. MNPs Characterization

The size and morphology of the MNPs were observed by scanning electron microscopy (SEM), using an FEI Nova NanoSem200 with a low vacuum detector. A PANalytical X-ray diffractometer model Empyrean of Malvern with a K-Alpha Cu anode of 1.54 nm at an

amperage of 40 mA and a 45 kV voltage, with a scanning step of 0.02 in 20 degrees, was used to know the crystal structure of the MNPs. The specific surface area was determined by the Brunauer, Emmett, and Teller (BET) method, using the Quantachrome Nova Corporation 1000 series equipment. The samples were degassed in a vacuum at 150 °C for 10 h. Furthermore, photoelectron spectroscopy (XPS) analyses were carried out with a Thermo Scientific Escalab 250Xi instrument. During analysis, the base pressure was ~ 10^{-10} mbar, and the photoelectrons were generated with the Al K α (1486.68 eV) X-ray source with a monochromator and a spot size of 650 µm. The X-ray voltage and power were 14 kV and 350 W, respectively. The high-resolution spectra's acquisition conditions were 20 eV pass energy, 45° take-off angle, and 0.1 eV/step. The recorded photoelectron peaks were analyzed with the Avantage Software V 5.4. The magnetic properties of MNP powder samples were analyzed at room temperature (26 °C) with an AGM MICROMAG magnetometer. Z potential (PZ) was determined as a pH function with distilled water with a Microtrac Zeta Check with a 400 µm piston, five times for each sample.

2.3. Adsorption Experiments

Adsorption experiments were performed to eValuate the MNPs' arsenic adsorption capacities. Kinetic experiments were carried out at different adsorbent doses (0.01 and 0.1 g/L), different contact times (1, 15, 30, 60, and 90 min), and different pH (6, 7, 8, and 8.5) by shaking the solution (480 rpm) with an initial As concentration of 45 μ g/L at room temperature.

MNPs' separation was carried out through the #42 filter, and the total As final concentration was determined by a GBS atomic absorption spectrophotometer (GBC XplorAA Dual model Avanta P) coupled to a hydride generator (HG-AAS) with flame (air-acetylene). Three milliliters of concentrated HCl and 3 mL of Kl were added to the samples and allowed to stand for 3 h before the analysis, according to the method's procedure.

Finally, ion competition experiments were carried out at an initial As(III) concentration of 40 μ g/L. The solution was prepared using NaAsO₂ (J.T. Baker) as an analytical grade reagent, dissolved in deionized water, and the different cations were added separately.

The groundwater As adsorption efficiency was eValuated in natural groundwater. Samples were acquired from the San Luis well (Durango, México). Test samples of 50 mL with an adsorbent dose of 0.1 g (CoFe₂O₄/MnFe₂O₄) were used, and the total contact time with shaking (480 rpm) was 60 min. Then, the MNPs were filtered by magnetic filtration, and the flasks were labeled for their analysis. The groundwater characteristics are given in Table 1.

Table 1. Physicochemical water characterization.

Parameter	Value
As μg/L	32.00
pH	8.04
Conductivity (µs/cm)	542.50
Fluoride (mg/L)	4.12
Na^+ (mg/L)	46.14
K^+ (mg/L)	7.94
Ca^+ (mg/L)	61.00
Mg^+ (mg/L)	1.54
NO_{3-} (mg/L)	37.50
Cl^{-} (mg/L)	23.14
CO_3^{2-} (mg/L)	0
HCO_3^{-} (mg/L)	138.60
$SO_4 (mg/L)$	59.76
Total alcalinity (mg $CaCO_3/L$)	138.60
Hardness (mg/L)	<5

3. Results

3.1. Characterization of CoFe₂O₄ and MnFe₂O₄ Nanoparticles

The size and morphology of the two magnetic nanoparticles synthesized were determined by scanning electron microscopy (SEM). According to the images and histograms, the samples consist of nanoparticles with relatively uniform size and quasi-spherical morphology (Figure 1a–d).



Figure 1. Scanning electron microscopy images, MNPs morphology: CoFe₂O_a (a,b), MnFe₂O₄ (c,d).

The size distribution was calculated using ImageJ software, and average sizes of 22 and 38 nm were obtained for $CoFe_2O_4$ and $MnFe_2O_4$, respectively. Regarding the BET results, the specific surface area values for $CoFe_2O_4$ and $MnFe_2O_4$ were 198.6 and 188.8 m²/g, respectively. Moreover, the pore size of both MNPs was around 5.8 nm. According to the IUPAC (International Union of Pure and Applied Chemistry), mesoporous materials are found in the range from 2 to 50 nm; therefore, the MNPs synthesized in this study are mesoporous materials.

The XRD patterns of CoFe₂O₄ and MnFe₂O₄ are shown in Figure 2. Figure 2a shows the diffraction peaks for the CoFe₂O₄ sample, located at the 2 θ values of 18°, 30°, 36°, 43°, 57°, and 62° with the respective crystal planes (111), (220), (311), (400), (511), and (400), corresponding with the card JCPDS-22-1086 [15]. Figure 2b corresponds to the MnFe₂O₄ sample, and the peaks 2 θ to 30.31°, 36.60°, 44.57°, 58.68°, 57.12°, and 65.78° are indexed to planes (220), (311), (400), (511), and (440), matching the cubic structure centered on the face of MnFe₂O₄, according to the International center diffraction data card, JCPDS-742403 [22].



Figure 2. XRD patterns for (a) CoFe₂O₄ and (b) MnFe₂O₄.

In order to obtain the composition and chemical states of the MNPs, XPS measurements were carried out. As a result, the full survey spectra of $CoFe_2O_4$ and $MnFe_2O_4$ confirm the presence of Co, Fe, Mn, and O elements, as shown in Figure A1.

The high-resolution spectra of the samples are shown in Figure 3a-f. The energy levels to analyze correspond to Co 2p, Fe 2p, and O 1s for the CoFe₂O₄ sample, and Mn 2p, Fe 2p, and O1s for the MnFe₂O₄.



Figure 3. The high-resolution XPS spectra for (a–c) CoFe₂O₄ and (d–f) MnFe₂O₄.

The high-resolution Co 2p spectrum shown in Figure 3a can be fitted with two spinorbit doublets and their corresponding satellite peaks. The binding energy of Co $2p_{3/2}$ is found at 781.23 eV with a satellite peak at 788.24 eV, while the binding energy of Co $2p_{1/2}$ is located at 796.73.4 eV and its satellite peak at 803.74 eV. Thus, the existence of Co²⁺ is suggested [23]. For the Fe 2p (Figure 3b), the binding energy at 711.64 and 724.44 eV are assigned to Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively, confirming the presence of Fe³⁺ in octahedral sites [23]. Furthermore, the signal at 714.80 is assigned to Fe³⁺ as tetrahedral species [23].

For the high-resolution O 1s spectrum (Figure 3c), three signals are observed, whereby the main peak at 530.02 eV is ascribed as a metal-oxygen bond and the remaining two peaks at 531.53 eV and 533.64 eV are assigned to oxygen from functional groups [23].

The high-resolution XPS spectra for $MnFe_2O_4$ are presented in Figure 3d–f. The XPS fitted spectra for Mn 2p (Figure 3d) reveal two main peaks located at 642.38 eV, which corresponds to Mn $2p_{3/2}$ and at 654.08 eV attributed to Mn $2p_{1/2}$, and the separation between these two peaks is 11.7 eV, which corresponds to Mn^{2+} [24,25]. Fe 2p spectra (Figure 3e) show two main peaks at 711.29 eV and 724.89 eV, which are attributable to Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively, of Fe³⁺ [25,26]. XPS fitted spectra of O1s in Figure 3f show three main peaks at 529.89 eV attributed to Fe-O or Mn-O, at 530.98 eV and 532.05 eV, ascribed to C-O and C=O, respectively [25].

The MNPs hysteresis cycles were investigated to check the magnetization saturation degree. Figure 4a shows $CoFe_2O_4$ and $MnFe_2O_4$ powders results, where 58.80 and 48.40 emu/g were obtained, respectively. The high crystalline quality could be related to their superparamagnetic behavior [26]. In the absence of an external magnetic field, these particles have zero magnetization and less tendency to agglomerate [27] because the magnetization values remain and the field coercive is negligible.



Figure 4. (a) Hysteresis cycle of CoFe₂O₄ and MnFe₂O₄, and (b) Zeta potential as a function of pH of CoFe₂O₄ and MnFe₂O₄.

Hence, these MNPs could be separated from the solution by applying an external magnetic field, making their recovery easy. When the external magnetic field is removed, these nanoparticles will quickly disperse.

Figure 4b shows the synthesized MNPs zeta potential results as a function of the pH. For CoFe₂O₄ and MnFe₂O₄, the difference between the pH values over the zeta potential is negligible. The MNPs' charge at pH 2 is positive. On the other hand, for pH of 4, 6, 8, 8.5, and 10, the MNPs' surface charge is negative; so, the isoelectric point of these materials would be at pH 2. Furthermore, at pH > 4, the slope of the line towards the negative charges is considerably increased. According to these results, the adsorption of positive ions in these materials would be fostered from pH > 2 because the surface charges are partially negative and will promote equilibrium with the MNPs' positive surface charge. This positive charge could be due to the presence of \equiv Fe-OH²⁺ groups on the surface, while the negative surface charge of the MNPs particles above pH > 2 could be due to the \equiv Fe-O- groups [28].

3.2. Adsorptions Experiments

Adsorption experiments were performed with two solutions. The first one was prepared with deionized water at an initial As concentration of 45 μ g/L, and the second one was the groundwater from the San Luis well (Durango, Dgo., Mexico).

Figure 5 shows the As(III) removal efficiency at two different adsorbent concentrations (0.01 and 0.1 g/L). The results show the adsorption capacity as a function of the adsorbent concentration, and the adsorption process is strongly linked to the surface area available for the adsorption [29,30]. With an adsorbent dose of 0.1 g/L, As(III) removal reaches 97% with CoFe₂O₄ and 94% with MnFe₂O₄. Besides, removal efficiency with the less adsorbent dose (0.01 g/L) was 85 and 78%, with CoFe₂O₄- and MnFe₂O₄, respectively.



Figure 5. As adsorption with the two nanoparticles (CoFe₂O₄ and MnFe₂O₄) at different contact times and adsorbent doses: (**a**) 0.01 g/L and (**b**) 0.1 g/L.

Yang and Yin (2017) studied mesoporous $CoFe_2O_4@MIL-100$ (Fe) MNPs, with an average diameter of 260 nm, and their results have shown rapid and selective As adsorption (143.6 mg/g) [31], similar to the results shown in this study. Moreover, Zhang et al. (2011) reported that As adsorption with $CoFe_2O_4$ and $MnFe_2O_4$ depends on several parameters, such as pH, initial As concentration, contact time, and the presence of interfering ions. The maximum adsorption capacities that they obtained for As(III) and As(V) were 94 and 90 mg/g with $MnFe_2O_4$, and 100 and 74 mg/g with $CoFe_2O_4$ [32].

In addition, with a less adsorbent dose (CoFe₂O₄, 0.2 g/L), Zhang (2010) reported 90% (As(III)) maximum removal efficiency in twelve hours [33]. In the present study, after 30 min with the adsorbent dose of 0.1 g/L, a final As concentration below 25 μ g/L (Mexican regulations for drinking water [34]) was reached with both MNPs. In contrast, Podder (2015) reports 86 % As(III) removal with MnFe₂O₄ after 80 min and an adsorbent dose of 2 g/L [34]. Furthermore, Iconaru (2016) reported maximum removal efficiency of 70% after 24 h of contact time with Fe₃O₄ (2 g/L) for As(III) [35].

Figure 6 shows the effect of contact time at different initial As(III) concentrations with both MNPs ($CoFe_2O_4$, $MnFe_2O_4$) on As(III) removal. As we can see, the arsenic removal with both nanoparticles was independent of the initial arsenic concentration, achieving an As(III) adsorption higher than 90 % in all cases in the first 10 min of treatment. Thus, in a contact time of 50 min, up to 95% of the arsenic can be adsorbed for concentrations of 45



and 50 (μ g/L). The adsorbate removal was performed quickly in the early stages; then, the adsorption rate gradually declined until the equilibrium was reached in each case.

Figure 6. As(III) adsorption with respect to time (in minutes) of adsorbate-adsorbent contact of (a) CoFe₂O₄, (b) MnFe₂O₄.

Therefore, the reduction curves were simple, smooth, and continuous, which led to equilibrium and the possibility of multilayer coverage on the adsorbent surface [31].

The maximum removal of As(III) ions with $CoFe_2O_4$ and $MnFe_2O_4$ (98% and 95%, respectively) was achieved after 30 min with an initial As concentration of 45 µg/L. Podder et al. (2015) reported that the maximum adsorption of As(III) ions (Operating conditions: Ci 4 mg/L, pH: 7.0 As(III)) was achieved after 80 min (85%) with SD/MnFe₂O₄ composites [36]. In this study, less contact time was enough to achieve removal efficiency (98%) reported by Podder et al. (2015).

The pH could be an important factor to take into account in the adsorption processes. So, in this study, the pH effect was eValuated. Figure 7 shows the effect of pH on the adsorption process with the MNPs of $CoFe_2O_4$ and $MnFe_2O_4$. A similar pattern of As adsorption in all pH assayed was observed. The maximum adsorption was reached after 10 min, in all cases, probably due to the MNPs negative surface charge, -90 mV for $CoFe_2O_4$ and -98 mV for $MnFe_2O_4$. At the pH range assayed (6, 7, 8, and 8.5), the H_3AsO_3 is positively charged, which allows us to explain the high efficiency of the As (III) removal.

The As(III) adsorption capacity remained similar in the range of the pH studied; this is possible because of the lack of competition with the hydroxyl groups (OH-) that were generated during the adsorption processes [29], keeping the MNPs' adsorption sites active as well as the non-deprotonation [7]. Alternatively, this is probably because it involves a two-step ligand exchange reaction: First, the hydroxyl group of the metal hydroxide is protonated; then, the H₂O ligand is replaced with the oxyanion, so the adsorption is affected by protonation of the pH-dependent metal hydroxide surfaces because the affinity differences of the adsorption between the oxyanion species are generally small. This is usually attributed to the metal hydroxides' surface deprotonation with the increased pH [37]. Thus, the surfaces of our MNPs play an essential role in the electrostatic interaction for the ligands exchange.



Figure 7. pH effect on the adsorption with $CoFe_2O_4$, $MnFe_2O_4$, (**a**) pH 6, (**b**) pH 7, (**c**) pH 8, and (**d**) pH 8.5. As(III) Ci 45 μ g/L.

On the other hand, at pH 8, the highest adsorption capacity was reached with $CoFe_2O_4$ (Figure 8c), achieving a removal efficiency of 99.7%. Furthermore, it is important to notice that more than 90% adsorption is achieved with the two synthesized nanomaterials, and the results can be attributed to the protection of negatively charged sites on the surface of the MNPs.



Figure 8. Contact time (1, 5, and 10 min) effect at different pH on the As(III) adsorption with $CoFe_2O_4$ and $MnFe_2O_4$ at (a) pH 6, (b) pH 7, (c) pH 8, and (d) pH 8.5, with an initial As concentration of 45 μ g/L.

As shown in Figure 8, during the first minute of contact, As ions removal achieves 80% in the pH range studied, and the greatest As removal was observed during the first

10 min. So, As removal through these nanomaterials is swift, and it could be attributed to the strong affinity of the MNPs iron ions. However, it could also be due to the adsorbents' high specific surface area, which had enough active sites to carry out the adsorption.

Some authors [38,39] reported removal efficiencies around 85% in contact times between 30 and 120 min. However, in this study, the MNPs synthesized showed higher As(III) removal efficiency in less time (10 min), eVen at different pH.

As Figure 8 shows, the As(III) adsorption efficiencies for the two nanomaterials were more than 90%. eVen at the first 5 min, the final As concentration was below the limit proposed by the World Health Organization (WHO, 10 μ g/L). Moreover, Figure 8 shows that the MNPs' adsorption capacity is independent of the solution pH, at least in the range of 6 to 8.5. Likewise, it can be noticed that the As adsorption rate during the first minute is higher than the rate obtained from minute 2 onwards and decreases as time goes by. This may be because the available adsorption sites become saturated as time passes.

Natural water composition varies depending on the sampling site, therefore the ions in the natural water are characteristic of the region and can be a significant factor in the water treatment process. To determine if the occurrence of these ions would affect the MNPs' arsenic adsorption efficiency, well water samples were taken, and the concentration of the majority cations found in groundwater samples was Na (as NaCl, 60 mg/L), K (as KCl, 57 mg/L), Ca (as CaCl, 52 mg/L), and Mg (as MgCl, 2 mg/L).

Figure 9a shows the competing cations found in Durango's groundwater (Na⁺, K⁺, Mg⁺, and Ca⁺) and their effect on As (III) adsorption, using CoFe₂O₄. eVen if the present ions can compete directly for the surface adsorption sites and indirectly influence the As (III) adsorption by altering the electrostatic charge of the solid surface, their presence did not have a detrimental effect on As (III) adsorption capacity of CoFe₂O₄. In contrast, competition with Mg+ was observed when MnFe₂O₄ was used for As (III) removal, and this could be attributed to both similar charge properties at the working pH (pH 8). However, this was observed only in the presence of Mg⁺ and not for the other cations (Na⁺, K⁺, and Ca⁺) (Figure 9b).



Figure 9. Competing ions removal and effect on the As (III) removal (Ci 33 μ g/L) with (**a**) CoFe₂O₄ and (**b**) MnFe₂O₄ as the absorbent.

As adsorption efficiency in groundwater samples was calculated from the maximum adsorption capacity (Qm), the results are presented in Figure 10 for $CoFe_2O_4$. The initial sample pH was 7.9, and the final pH was 8.1. The pH is a significant variable in the adsorption process because it can cause interference between the ions in the solution and the MNPs' surface [29].



Figure 10. As adsorption in groundwater using CoFe₂O₄ and MnFe₂O₄.

The maximum adsorption occurs in the first ten minutes until a value of 89% is reached at 15 min; this could be due to the presence of HCO_3^- , which could generate competition for As (III) adsorption.

The As adsorption with MnFe₂O₄ decays by 1% compared to the results achieved with CoFe₂O₄. The equilibrium was reached after 30 min with a final adsorption percentage of 88%, and a final As concentration (C_F) below 5 μ g/L, making MnFe₂O₄ a suitable material for water treatment technologies for human consumption, because the final As concentrations achieved were in accordance with the NOM-127-SSA1-1994 (2000) and the World Health Organization limits. Therefore, CoFe₂O₄ and MnFe₂O₄ are highly promising MNPs for groundwater As removal in compliance with water quality As-permissible limits.

3.3. Adsorption Kinetics Study

In this study, As (III) adsorption kinetics were performed to explore the adsorption rate. Figure 11a shows the changes of As (III) concentration in the solution against time for $CoFe_2O_4$ and $MnFe_2O_4$. The As (III) adsorption was fast in the first 10 min, then it slowed down until the equilibrium was reached, at 30 min. The quick initial As (III) adsorption could be due to the nanoscale particle size of the adsorbents, since the fine particles favored the As (III) diffusion from the solution towards the active sites of the adsorbents [40]. First- and second-order equations [41] were used to describe the As (III) adsorption in these MNPs, and the best linear fit was obtained with the second-order reaction model (Figure 11b).



Figure 11. (a) Adsorption kinetics of As (III) for CoFe₂O₄ and MnFe₂O₄, (0.1 g/L) pH 8; (b) second-order kinetic graph for As (III).

Kinetic Model	Equation	Constant	Value CoFe ₂ O ₄	Value MnFe ₂ O ₄
First order	$Ln Ct = Ln Co - K \times t$	К (R ²)	17.47 (0.8576)	16.75 (0.8532)
Second order *	$\tfrac{1}{C_t} = K.t + \tfrac{1}{C_o}$	K (R ²)	$\begin{array}{c} 6.66 \times 10^{113} \\ (0.99) \end{array}$	$8.33 imes 10^{27}$ (0.99)

The second-order rate constants for As (III) adsorption with $CoFe_2O_4$ and $MnFe_2O_4$ are shown in Table 2.

Table 2	Kinetic	constants.
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* Where Ct (μ g/L) is the concentration of As in the solution at time t (minutes), Co (μ g/L) is the initial concentration of As, and K (L/ μ g,min) is the rate constant of adsorption.

The As adsorption isotherms were carried out at pH 7 with initial As concentrations (Ci) of 25, 45, 65, and 75 μ g/L in 100 mL; the adsorbent dose was 0.1 g/L, and the contact times were 1, 5, 10, 30, and 60 min. The Langmuir and Freundlich models were used to adjust the data, and the correlation coefficient (R²) was used to compare and determine the best model of adjustment. The adsorption isotherms of As (III) ions on MNPs are shown in Figure A2. Table 3 shows the parameters related to the Langmuir and Freundlich isotherms for the two MNP samples.

Table 3. Values for the Langmuir and Freundlich isotherms.

	MNPs –	Langmuir		Freundlich		
		Qm (mg/g)	R ²	KF (mg/g)	n	R ²
As (III)	CoFe ₂ O ₄	250	0.99	1.27	0.28	0.98
	MnFe ₂ O ₄	238.1	0.99	1.38	0.29	0.98

The regression coefficient (R^2) obtained in both cases was higher than 0.99, which indicates that the isotherm models were adequate to describe the adsorption behavior of the As ions on the MNPs; eVen for the Freundlich model, the R^2 was 0.99, which suggests the occurrence of a multilayer/physical adsorption process. Thus, the application of the Langmuir isotherm model is limited to monolayer adsorption on the adsorbate-adsorbent surface. On the other hand, the Freundlich model is an empirical equation based on the multilayer adsorption of an adsorbate on heterogeneous surfaces.

The maximum adsorption capacity was calculated from the Langmuir isotherm and was 250 for $CoFe_2O_4$ and 238 mg/g for $MnFe_2O_4$. The synthesized nanomaterials of $CoFe_2O_4$ and $MnFe_2O_4$, which possess a high ion adsorption capacity of As (III) ions, were convenient for the As (III) adsorption, likewise with an easy recovery with magnetic separation.

In the subsequent calculation, a substantial adjustment to both models is discernible ($R^2 = 0.99$). The maximum adsorption capacity for short times does not change significantly in the Langmuir model, at 222.22 and 105.26, mg/g for CoFe₂O₄ and MnFe₂O₄, respectively. In the Freundlich model for MnFe₂O₄ (2.04 mg/g), a sudden change is observed, and CoFe₂O₄ remains at 1.38 mg/g. These subsequent studies demonstrate that the synthesized materials possess a high adsorption capacity for metal ions, specifically As (III), in shorter contact times than those reported [38–42].

Proposed Mechanism

Based on the operating conditions and isotherms, the $CoFe_2O_4$ adsorption capacity was greater than that for $MnFe_2O_4$. This result can be explained by the material's properties, such as the smaller size and greater surface area. When cobalt oxide (CoO) comes in contact with water, it could cause water hydrolysis (water molecule dissociation) because iron oxides' pH is basic. When water is dissociated, the OH⁻ ions bind to the metal (Co and Mn), and the H⁺ ions bind to oxygen (hydroxylation), causing a surface change on the adsorbent surfaces depending on the pH. Considering the reactions that take place, reaction 1 (Rx 1) represents the hydrated adsorbent surface, and depending on the pH, the adsorbent surface can be either positively or negatively charged; reaction 2 represents what happens with the adsorbent surface charge in the basic medium.

$$CoO(OH)_{s} + H_{2}O_{L} \rightarrow CoFe^{2} + 3OH^{-}$$
(Rx. 1)

$$CoFe(OH)_3 \leftrightarrow CoFe(OH)_2^+ + OH^-$$
 (Rx. 2)

CoO could be replaced by MnO for the other adsorbents studied.

Furthermore, according to the As adsorption mechanism (physisorption), the As ions were adsorbed to the surface of $CoFe_2O_4$ by weak forces that include the oxygen–metal bridge and van der Waals [42]. In addition, it was reported that electron-rich atoms such as oxygen could interact with a metal/oxide site to form an intermediate bridge called the oxygen–metal bridge [43]. Because these types of forces are weak, adsorption on these materials can be reversible.

4. Discussion

The use of magnetic nanoparticles provides an opportunity to solve problems derived from water contamination, including solutions related to bacteria, viruses, and pesticides removal.

The As adsorption capacities in MNPs are firmly attributed to their properties, for instance their surface area is one of the main factors that assist As adsorption. $CoFe_2O_4$ and $MnFe_2O_4$ presented higher surface area values (198.6 and 188.8 m²/g, respectively) to which the best performance in terms of the adsorption capacity of As ions in groundwater is attributed. Previous works [15–21] report 96% removal of As using adsorbents such as $CoFe_2O_4$ and 93% for $MnFe_2O_4$; however, the operating conditions are entirely different (0.2 g/L dose and in 8 h of contact time), which demonstrate that the MNPs reported in this work are more technically feasible. Magnetic adsorbents are ideal since they have a high adsorption capacity for As, and in terms of their magnetic properties, they are easy to separate from water. Additionally, the adsorption of As (III) for these MNPs is very fast, reaching the equilibrium time in less than 30 min; experiments by Saidur R et al., 2010 report the equilibrium within 24 h.

5. Conclusions

The adsorption capacity of $CoFe_2O_4$ and $MnFe_2O_4$, synthesized by the chemical coprecipitation method, supports their potential application for As (III) removal from water to below the WHO recommended value of 10 µg/L.

In this study, CoFe₂O₄ and MnFe₂O₄ showed excellent adsorption capacities. This could be due to the several surface hydroxyls groups and other morphological characteristics, such as their size and greater surface area, creating more adsorbing sites.

The zeta potential change in the MNPs at pH > 2 implies the formation of groups with a negative charge on the surface of the MNPs. The pH has no significant effect on As (III) adsorption in the worked range.

As a promising perspective, MNPs demonstrated a high capacity to remove As from water, eVen at the presence of several ions (as Ca, Mg, Na, and K, among others), allowing their potential application in continuous flow systems. Moreover, arsenic can be desorbed from the MNPs with a NaOH solution, and the adsorbents could be separated from the solution using magnetic filtration processes. This issue should be addressed in upcoming work.

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Appendix A



Figure A1. Wide XPS scan.





Figure A2. Langmuir and Freundlich isotherms for the MNPs samples.

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