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The Effects of Magnetite Iron Oxide Nanomaterials on Arsenic Adsorption and the Freshwater Medicinal Leeches *Hirudo verbana*

Hamdi EKİZOĞLU [1]✉ **Erdal YILMAZ** [2] **İsmail ÖÇŞOY** [3]

[1] Erciyes University, Science Institute, Zootechnics, Kayseri/ Türkiye
[2] Erciyes University, Faculty of Veterinary Medicine, Department of Aquatic Animal Disease, Kayseri/ Türkiye
[3] Erciyes University, Department of Analytic Chemistry, Kayseri/ Türkiye

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Abstract: In the present study, nano sized Fe3O4 particles (NPs) and composites (NCs) were prepared by a simple solvo-thermal method in ethylene, di-ethylene or tetraethylene glycol solutions for the removal of arsenic from tap water. Adsorption experiments were conducted by adding Fe3O4 NPs, and Fe3O4- graphene oxide (GO), Fe3O4-GO -ethylene diamine tetra acetic acid (EDTA) and Fe3O4-GO-Glutatyon (GLU) NCs to the tap water containing 50 ppm standard arsenic acid solution (H3AsO4). The best arsenic adsorption capacity (81.39 %, 72.00 mg As/ g NPs) was obtained from bare Fe3O4 NP's group. In the second stage, it was aimed to investigate the effects of Fe3O4 NPs on medicinal leeches (Hirudo verbana) as experimental animals. In this stage, the effect of the different concentrations (0, 0.25, 0.75 and 1 mg/L) of Fe3O4 NPs on the leeches H. verbana and heavy metal accumulations were determined at the end of 96 hours. Different doses of Fe3O4 NPs had no adverse effects on survival of the medicinal leeches, although heavy metal accumulations of the leeches were found different significantly compared to the control group (P<0.001). In conclusion, Fe3O4 NPs showed the best performance with respect to arsenic removal from tap water and the biocompatibility tests. These findings highlight the dual potential of Fe_3O_4 nanoparticles in water remediation and ecological safety, offering a promising route for sustainable environmental applications

Keywords: Magnetite nanoparticles, Arsenic removal, Hirudo verbana, Water remediation, Biocompatibility

Manyetit Demir Oksit Nanomalzemelerin Arsenik Adsorpsiyonu ve Tatlı Su Tıbbi Sülükleri *Hirudo verbana* Üzerindeki Etkileri

Özet: Bu çalışmada, musluk suyundan arseniği uzaklaştırmak için etilen, dietilen veya tetraetilen glikol çözeltilerinde basit bir solvotermal yöntemle nano boyutlu Fe3O4 parçacıkları (NP'ler) ve kompozitleri (NC'ler) hazırlandı. Adsorpsiyon deneyleri, 50 ppm standart arsenik asit çözeltisi (H3AsO4) içeren musluk suyuna Fe3O4 NP'leri ve Fe3O4-grafen oksit (GO), Fe3O4-GO-etilendiamin tetraasetik asit (EDTA) ve Fe3O4-GO-Glutatyon (GLU) NC'leri eklenerek gerçekleştirildi. En iyi arsenik adsorpsiyon kapasitesi (%81.39, 72.00 mg As/g NP), saf Fe3O4 NP'leri grubundan elde edildi. İkinci aşamada, Fe3O4 NP'lerinin tıbbi sülükler (Hirudo verbana) üzerindeki etkilerinin deneysel hayvan olarak araştırılması amaçlandı. Bu aşamada, Fe3O4 nanopartiküllerinin farklı konsantrasyonlarının (0, 0.25, 0.75 ve 1 mg/L) H. verbana sülükleri üzerindeki etkisi ve ağır metal birikimleri 96 saat sonunda belirlendi. Fe3O4 nanopartiküllerinin farklı dozlarının tıbbi sülüklerin hayatta kalması üzerinde olumsuz bir etkisi olmadığı, ancak sülüklerin ağır metal birikimlerinin kontrol grubuna kıyasla anlamlı derecede farklı olduğu (P <0.001) bulundu. Sonuç olarak, Fe3O4 nanopartikülleri, musluk suyundan arsenik uzaklaştırılması ve biyo-uyumluluk testleri açısından en iyi performansı gösterdi. Bu bulgular, Fe3O4 nanopartiküllerinin su arıtımı ve ekolojik güvenlikteki ikili potansiyelini vurgulayarak, sürdürülebilir çevresel uygulamalar için umut vadeden bir yol sunmaktadır.

Anahtar Kelimeler: Manyetit nanopartikülleri, Arsenik uzaklaştırma, Hirudo verbana, Su arıtımı, Biyo-uyumluluk

1. Introduction

Arsenic pollution either occurs in nature from geological processes such as the weathering of rocks, volcanic emissions, and geothermal activities, or as a result of anthropogenic activities such as agricultural (via pesticides and herbicides), mining, and industrial wastes (Gibbons and Gagnon 2010). Arsenic rapidly accumulates in the soil, water, and sediment, posing a threat to the environment and living organisms (Shaji et al. 2021; Prasad Ahirvar et al. 2023). Arsenic concentrations in ground and surface waters have been found to range from 100 to 5.000 µg/L and this widespread contamination of As emerges an important global environmental problem (Zhang et al. 2022). Not only humans, arsenic contamination in water has affected aquatic animals and plants to a great extent. In particular, the presence of As in aquatic systems has already shown to induce toxic effects in aquatic animals such as bivalves (Freitas et al. 2018), mussels (Coppola et al. 2018), algae, crustaceans and fish (Federici et al. 2007; Torre et al. 2015; Fabrega et al. 2011; Guan et al. 2018) in earlier studies.

✉: hamza_ekiz@hotmail.com

Treatment of arsenic-polluted water with improved or completely new technologies, such as nanomaterials, to provide a safe environment to aquatic animals is an urgent issue in recent years. The use of iron oxide nanoparticles has exhibited excellent properties with high removal efficiency, lower cost, and simpler operational processes compared to other alternative methods. These nanomaterials are widely preferred to treat wastewater by removing heavy metals due to their exceptional physical and chemical characteristics such as strong adsorption, superparamagnetic nature, high surface area, biodegradability and lower toxicity (Maksoud et al. 2020; Gautam et al. 2015). Although nanoparticle adsorption serves an effective technique for removing of As from the water (Fang et al. 2022; Moradi et al. 2023), these NPs can accumulate in aquatic environments after their applications and affect the living organisms. Thus, making assessment of potential hazardous impacts of NPs on inhabiting organisms has been crucial.

In the present research, it was aimed to synthesize different sizes of iron oxide nanomaterials to test the adsorption processes of arsenic from the freshwater. In this concept, arsenic adsorption capacities of Fe3O4 NPs, Fe3O4-GO NCs, Fe3O4-GO-EDTA NCs and Fe3O4-GO-GLU NCs were determined. Also, the effects of iron nanoparticles having the highest arsenic adsorption capacity on medicinal leeches (Hirudo verbana), as an aquatic animal, were investigated by the biocompatibility tests. In this concept, Conservation Evidence does not yet cover the topic, and no individual study exists.

2. Materials and Methods

2.1. Synthesis of Magnetite Fe3O4 NPs

Nano- and submicro-sized Fe3O4 particles were prepared by a simple solvothermal method in ethylene, di-ethylene or tetraethylene glycol solutions with the help of microwave irradiation. 50 mg of Fe(acac) was sonicated to be homogenous in 10 mL of ethylene glycol, di-ethylene or tetra-ethylene glycol followed by the addition of 200 mg sodium acetate and 1 g 1.6 hexadamine hamedan. These mixtures were placed in a seperate 100 mL Teflon reaction vessel (XP-1500 Plus), heated in a CEM Mars 5 microwave oven to the required temperature (for ethlylene and di- ethlylene, and tetra- ethlylene methods were 200 and 240 °C, respectively) and maintained at this temperature for 6 hours. After the reaction, the vessel was cooled to room temperature and a black precipitate was collected with the help of a permanent magnet. Subsequently, the obtained nanoparticles were washed with distilled water and ethanol for several times and dried in oven at 70 °C.

2.2. Synthesis of Magnetite Fe3O4-GO NCs

Firstly, 50 mg of Fe(acac) was sonicated to be homogenous in 10 mL of ethylene glycol, 10 mg graphene oxide (GO), followed by the addition of 200 mg sodium acetate and 1 g 1,6-hexadamine hamedan. These mixtures were placed in a 100 mLTeflon reaction vessel (XP-1500 Plus), heated in a CEM Mars 5 microwave oven to the required temperature (200 °C) and maintained at this temperature for 6 hours. After the reaction, the vessel was cooled to room temperature and a black precipitate was collected with the help of a permanent magnet. Subsequently, the obtained nanoparticles were washed with distilled water and ethanol several times and dried in an oven at 70 °C.

2.3. Synthesis of Magnetite Fe3O4-GO NCs in EDTA and glutathione

50 microliter of 0.1 M EDC was added to a PBS solution (10 mM, pH 7,4) to prepare a functional magnetite nanocomposite by using EDTA and/ or glutathione. This mixture was agitated to activate the carboxyl groups slowly during 30 minutes. Later, 20 microlitres of NHS and previously prepared nanoparticles were added, respectively. Shaking was continued for 4 hours to form final mixture. Black precipitate was collected with the help of a permanent magnet and the supernatant was removed.

2.4. Characterization of the Nanomaterials

The synthesized magnetite NPs and NCs were characterised using scanning electron microscope/energy dispersive spectroscopy (SEM/EDS), fourier-transform infrared spectroscopy (FTIR, Varian 3100) and laser doppler anemometry (Zetasizer Nano-ZS, Malvern Instruments), and dynamic light scattering (DLS) techniques for the determination of size/size distributions, surface charge and zeta potentials, respectively.

2.5. Batch/ Adsorption Experiments

Batch experiments were conducted to determine arsenic adsorption capacity of the nanoparticles and nanocomposites produced. These experiments were carried out using 50mL centrifuge tubes at ambient room temperature (20±2∘C) and pH 7 (pH was adjusted to 7 with nitric acid (HNO3, 70%, 99.999% trace metals basis). All reagents were purchased from Merck KGaA 64271 Darmstadt Germany. Magnetit NPs and/ or NCs containing 1 mg of Fe3O4NP, Fe3O4GO NCs and Fe3O4 GOEDTA NCs and Fe3O4 GOGLU NCs were added to 50 mL freshwater including 50 ppm arsenic acid standard solution (H3AsO4 in HNO3 containing 1000 mgL-1 As). All nanoparticle/ composites – arsenic suspensions were sonicated for 15 min with a probe sonicator. After 24h, arsenic and nanoparticles and/or nanocomposites mixtures were analysed in respect of residual arsenic by inductively coupled plasma mass spectrometry (ICP-MS Agilent 7900 model). The percentage of adsorption of arsenic was calculated with the following formula:

Where Ci: initial concentration of As, Cf: final concentration of As

2.6. Biocompatibility Tests

120 medicinal leeches (Hirudo verbana) avaraging 2-4 g were used for biocompatibility test. Medicinal leeches (H verbana) were obtained from a local leech farm (Cansuyu Tıbbi Sülük, Kayseri, Türkiye) and adapted to the laboratory conditions (at room temperature, 20±2∘C and pH 7,5). Biocompability tests were carried out in 8 plastic containers (1 L volume) each were stocked 15 leeches with four treatment groups and two replicates (15 x 4 x 2 = 120). 0.25, 0.75 and 1 mg of magnetite Fe3O4 NPs were added to the plastic containers to evaluate the effects on medicinal leeches during 96 hours. Magnetite Fe3O4 NPs were not given to the control group. At the end of this period, leeches were counted to calculate survival rates and dried to analyse the heavy metal contents by ICP MS device (Agilent 7900 model).

2.7. Statistical analyses

Statistical analyses were performed by using IBM-SPSS for Windows Release 25.0 programe (SPSS Inc, Chicago, IL, ABD). The suitability of normal distribution of the data were tested by histogram, q-q plots and Shapiro-Wilk. One-way ANOVA (alternatively, Kruskal-Wallis Test) was performed to detect the difference between treatment groups. Tukey and Bonferroni tests were used as Post-hoc test. If P value <0.05, differences between groups were accepted as significant.

3. Results

Characterisations and Adsorption Performance of the Nanomaterials

SEM analyses of magnetite Fe3O4 NPs synthesized with ethylene glicol (EG), diethylene glycol (DEG), and tetra-ethylene glicol (TEG) showed that nanoparticles had a round structure and an average size of 12-86, 19-100, and 13-52 nm, respectively (Figure 1a, 2a, 3a). Fe3O4- GO NCs synthesized with EG had also spherical structure and their sizes were between 11-32 nm (Figure 4a). In tap water, the aggregations of the Fe3O4 NPs synthesized with EG, DEG, TEG were observed by DLS, reaching an average size of approximately 1100, 1200, and 1200 nm, respectively (Figure 1b, 2b, 3b). In addition, Fe3O4-GO NCs synthesized with EG had a 970 nm DL spectrum (Figure 4b). Zeta potentials of magnetite Fe3O4 NPs and NCs varied between -10.4 mV – (-23.1 mV) (Figure 1c, 2c, 3c, and 4c). The best As removal performance from tap water was detected from the magnetite Fe3O4 NPs synthesized with EG (Table 1).

Table 1. Batch/ adsorption experiment results of the different NPs and NCs for arsenic

Treatment /solution	As removal (%)	As adsorption capacity (mg As/per g NP)
Fe_3O_4NPs / 50 ppm arsenic	81.39	72.00
Fe_3O_4-GO NCs / 50 ppm arsenic	70.45	62.00
Fe_3O_4-GO-EDTA NCs/50 ppm arsenic	56.82	50.00
Fe_3O_4-GO-GLU NCs /50 ppm arsenic	69.32	61.00

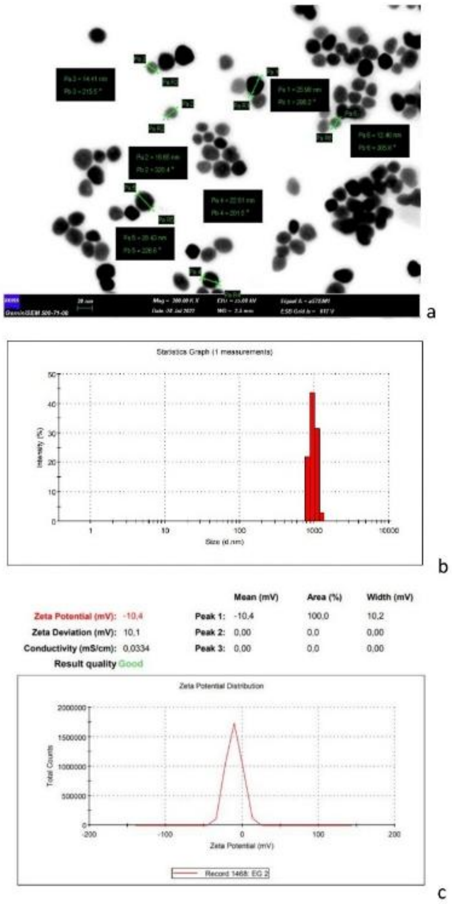

Figure 1. SEM views (a), DLS (b) (1100 nm), and zeta potential (c) (-10.4 mV) of magnetite Fe3O4 NPs synthesized with EG NPs had a round structure and an average size of 12-86 nm.

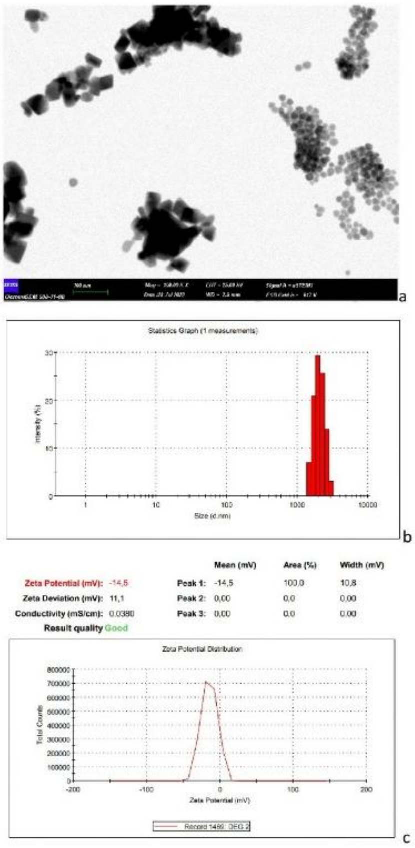

Figure 2. SEM views (a), DLS (b) (1200 nm), and zeta potential (c) (-14.5 mV) of magnetite Fe3O4 NPs synthesized with DEG NPs had a round structure and an average size of 19-100 nm.

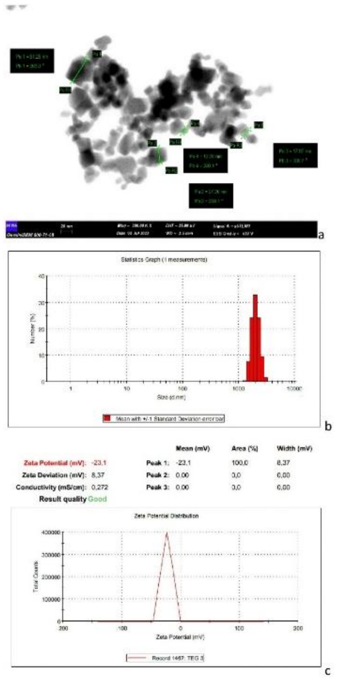

Figure 3. SEM views (a), DLS (b) (1200 nm), and zeta potential (c) (-23.1 mV) of magnetite Fe3O4 NPs synthesized with TEG NPs had a round structure and an average size of 13-52 nm.

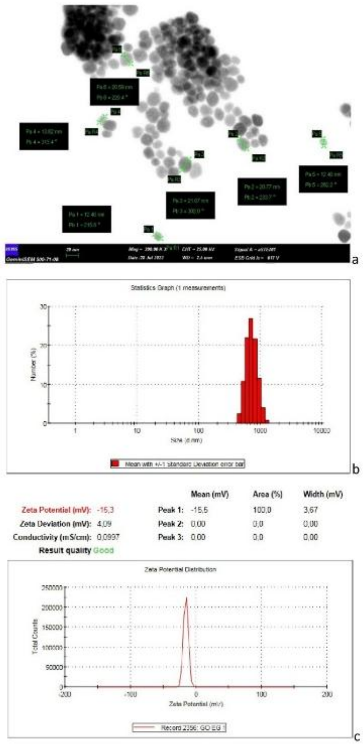

Figure 4. SEM views (a), DLS (b) (970 nm), and zeta potential (c) (-15.3 mV) of magnetite Fe3O4 NPs synthesized with EG NPs had a round structure and an average size of 11-32 nm.

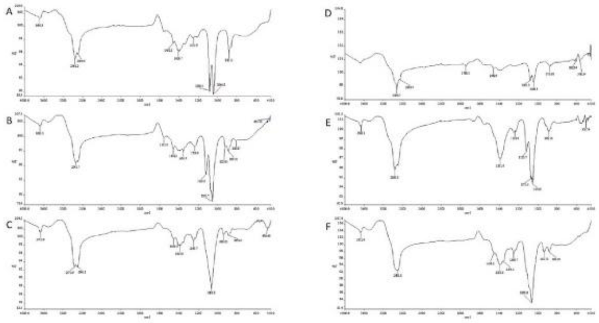

Figure 5. The Fourier Transform Infrared (FT-IR) spectrum of NPs (A-EG@Fe3O4, B-DEG@Fe3O4, C-TEG@Fe3O4 NPs) and NCs (D-EG@Fe3O4@GO, E-DEG@Fe3O4@GO and F-TEG@Fe3O4@GO NCs).

Table 2. Heavy metal concentrations of tissues of the medicinal leches (H verbana) exposed to different doses of Fe3O4 NPs*

Doses of Fe_3O_4 NPs					
Heavy metal (ppm)	Control	0.25mg/L	0.75mg/L	1mg/L	P value
Al	4.290±0.000^{a}	3.040±0.000^{d}	3.530±0.000^{b}	2.720±0.000^{c}	<0.001
Mn	2.590±0.000^{a}	3.340±0.000^{d}	3.170±0.000^{b}	2.740±0.000^{c}	<0.001
Fe	23.090±0.000^{a}	34.240±0.000^{d}	24.660±0.000^{b}	24.740±0.000^{c}	<0.001
Co	0.700±0.000^{a}	1.270±0.000^{d}	1.180±0.000^{b}	0.970±0.000^{c}	<0.001
Ni	0.580±0.000^{a}	0.620±0.000^{d}	0.660±0.000^{b}	0.530±0.000^{c}	<0.001
Cu	0.020±0.000^{a}	0.020±0.000^{a}	0.010±0.000^{b}	0.010±0.000^{b}	<0.001
Zn	9.240±0.000^{a}	16.690±0.000^{d}	10.060±0.000^{b}	10.220±0.000^{c}	<0.001
As	0.456±0.015^{a}	0.660±0.089^{c}	0.742±0.030^{b}	0.700±0.000^{bc}	<0.001
Cd	0.040±0.000^{a}	0.045±0.005^{d}	0.035±0.005^{b}	0.020±0.000^{c}	0.018
Hg	0.264±0.005^{a}	0.452±0.159^{d}	0.334±0.015^{b}	0.559±0.010^{c}	<0.001
Pb	0.324±0.005^{a}	0.154±0.005^{d}	0.199±0.010^{b}	0.169±0.010^{c}	<0.001

*Data were given as mean ± standard error, different letters with the same lines show the statistical differences between groups. Al: alüminium Mn: manganese Fe: ferrous Co: cobalt. Ni: nicel. Cu: copper. Zn: zinc As: arsenic. Cd: cadmium. Hg: mercury. Pb: lead

Table 3. Heavy metal concentrations of of the water in plastic container living medicinal leeches (H verbana) exposed to different doses of Fe3O4 NPs**

Doses of Fe_3O_4 NPs					
Heavy metal (ppm)	Control	0.25mg/L	0.75mg/L	1mg/L	P value
Al	0.030±0.000^{a}	0.003±0.001^{c}	0.020±0.000^{b}	0.002±0.001^{c}	<0.001
Mn	0.009±0.001^{a}	0.003±0.001^{c}	0.008±0.000^{b}	0.002±0.001^{c}	<0.001
Fe	0.034±0.005^{a}	0.006±0.000^{b}	0.034±0.005^{a}	0.006±0.005^{b}	<0.001
Co	0.007±0.000^{a}	0.002±0.000^{d}	0.005±0.000^{b}	0.001±0.000^{c}	<0.001
Ni	0.004±0.000^{a}	0.001±0.000^{c}	0.003±0.000^{b}	0.001±0.000^{c}	<0.001
Cu	0.002±0.000^{a}	0.001±0.000^{d}	0.003±0.000^{b}	0.006±0.000^{c}	<0.001
Zn	0.014±0.000^{a}	0.020±0.000^{d}	0.018±0.000^{b}	0.019±0.000^{c}	<0.001
As	0.010±0.004^{a}	0.001±0.000^{b}	0.003±0.000^{b}	0.008±0.004^{a}	<0.001
Cd	0.003±0.000^{a}	0.0004±0.003^{b}	0.004±0.000^{ab}	0.003±0.000^{a}	0.018
Hg	0.002±0.000^{a}	0.003±0.000^{d}	0.001±0.000^{b}	0.002±0.000^{c}	<0.001
Pb	0.003±0.000^{a}	0.001±0.000^{c}	0.003±0.000^{a}	0.002±0.010^{b}	<0.001

**Data were given as mean ± standard error, different letters with the same lines show the statistical differences between groups. Al: alüminium Mn: manganese Fe: ferrous Co: cobalt. Ni: nicel. Cu: copper. Zn: zinc As: arsenic. Cd: cadmium. Hg: mercury. Pb: lead

C-O ve C–H vibration peaks for EG@Fe3O4 NPs were determined as 1086 cm-1 and 2961 cm-1wavelenght. Tension vibrations of free O-H groups without hydrogen bonding for EG, DEG and TEG were observed between 3700 and 3640 cm–1. While vibration peaks of Fe-O were about 550-580 cm-1, DEG ve TEG@Fe3O4 NPs versions of the NPs were supressed and almost disappeared. Twist of C-H ve O-H for EG, DEG and TEG@Fe3O4 NPs was about 1458 cm-1 and C-N stretch peaks were observed arounds 1250 cm-1 due to the amine group (Figure 5). Concentrations of Mn, Fe, Co, Zn, As and Hg increased, while, Al, Cu and Pb concentrations decreased in H verbana tissues by different doses exposed of Fe3O4 NPs significantly at the end of the 24 h period (Table 2).

4. Discussion

Magnetite nanoparticles are promising adsorbents for the adsorption of arsenic due to high surface area, chemical stability, adequate surface distribution of reactive sites, selectivity towards arsenic species, good biocompatibility (Zhang et al. 2019; Nguyen et al. 2020; Nikić et al. 2021), and easy separation from water under external magnetic field conditions (Baig et al. 2021; Wang et al. 2019). Also, iron and iron oxides nanoadsorbents used in arsenic removal have attracted great attention due to reasons such as being economical, non-toxic, widely available in nature and environmentally friendly. (Hassan 2023; Wadhawan et al. 2020). Numerous iron-based nano adsorbents and processes have been developed to remove arsenic from the water in last decade. In one of these studies, Pham et al. (2020), used an iron hydroxide-based nanoparticles (IHNPs) to remove As (V) with the maximum removal capacity of 2.9 (mg As g-1 IHNPs). The most suitable conditions for the highest removal of As (V) from aqueous solution were pH 2, dose 50 g L-1, in 2 hours and at 30 °C temperature. In our experimental conditions (pH 7.5, dose 50 mg L-1, in 24 hours and at 20±2∘C) with the best adsorption capacity for arsenic was determined as 72.00 mg As g-1 Fe3O4NPs. Comparing to the earlier study we succeded the higher As adsorption by using lower amount of nanoparticle. From the current results, it could be stated that As asorption capacity of Fe3O4NPs were higher than that of IHNPs.

Iron oxide nanoparticles can be modified with different functional groups, alloying with other elements, and researchers in recent records have reported incorporation in several organic and inorganic substrates (Shah et al. 2020; Khalid et al. 2020). Bangari et al. (2019) synthesized magnetite-coated boron nitride nanosheets (BNNS-Fe3O4) and removed ~98.83% of As(V) from arsenic solution through exothermic chemisorption process. Furthermore, Bangari et al. (2020) showed that four folds increased the adsorption capacity of Fe3O4-functionalized boron nitride nanosheets (BNNS- Fe3O4 nanocomposite) compared with bare BNNSs for arsenic solution with the maximum adsorption capacity of 30.3 As mg g-1 at pH 8. Similarly, adsorption capacities of 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF6]) (ionic liquid)-modified magnetic graphene oxide (MGO-IL) were 160.65 mg/g and 104.13 mg g-1 for As (III) and (V), respectively (Zhang et al. 2019).

In addition, Tripathy et al. (2020) produced l-cysteine functionalized mesoporous magnetite (Fe3O4@Cy) nanosphere using a surfactant-assisted solvothermal method with enhanced stability and adsorption efficiency. The maximum adsorption capacities of Fe3O4@Cy nanoparticles were determined as 20.0 and 34.0 mg/g for As(III) and As(V) ions, respectively. Rowley and Abu-Zahra (2019) investigated the adsorption capacity of 3-aminopropyltriethoxysilane (APTES) Fe3O4 nanoparticles modified polyethersulfone (PES) nanocomposite membranes for As(V) removal from water. The adsorption capacity of the PES-A-Fe3O4 for As(V) gradually increased with an increasing percentage of APTES-Fe3O4 nanoparticles in PES membranes, and the maximum adsorption capacity (14.6 mg g-1) was obtained at 3 % APTES-Fe3O4.

The maximum adsorption capacities reported by Morales Amaya (2021) that were 250 mg g-1 for CoFe2O4 and 230 mg/g for MnFe2O4 MNPs. The adsorption capacities of CoFe2O4 and MnFe2O4 produced by the chemical coprecipitation method supports their potential application for As (III) below the recommended value of 10 µg L-1. This could be succeded by the several surface hydroxyls groups and other morphological characteristics, such as their size and greater surface area, creating more adsorbing sites. In addition, this higher As adsorpbance capacity obtained can be attributed to the bi-metalic nature of magnetite NPs. Thus, in the present study, using of bi-metalic MNPs with a more active surface could be recommended to increase As adsorbance capacity of the Fe3O4 NPs.

From studies related to this approach, Gurbuz et al. (2019) succeeded in removing up to 95.4% of arsenic from groundwater with the cryogel column. They reported that the poly (hydroxyethyl methacrylate (HEMA)-co- glycidyl methacrylate (GMA)) cryogel hybrid column adsorbed 11.44 of As (III) and 5.79 of As (V) mg g-1 polymer which equal 71.3-95.4% of total arsenic at pH 7, respectively. They managed to decrease the arsenic level to the drinkable levels by adsorption processes in groundwater (Gurbuz et al. 2019). Saif et al. (2019) stated that the highest monolayer saturation adsorption capacity of IONPs was 28.57 mg g-1. As(V) adsorption by polymer-supported IONPs best fit the Freundlich model, and maximum adsorption capacities of 34.4 mg g-1 and 40.3 mg g-1 were achieved for chitosan- and PVA–alginate-supported IONPs, respectively. PVA–alginate-supported IONPs were found to be more effective than the other adsorbents in respect of adsorption, stability, and reusability. Magnetite nanoparticles can also be synthesized by a simple and ecofriendly method using plant residues/ extracts, chitosan and zeolite. Nikic et al. (2019) used onion peel (MNp-OP) and corn silk extract (MNp-CS) were used in order to develop new low-cost adsorbents for arsenic removal from the water. Onion peel and corn silk extract are good phenolic candidates to reduce Fe3+. Magnetite nanoparticles were also synthesized by a conventional chemical process (MNp-CO) to compare with the natural counterparts. Maximal adsorption capacities of MNp-OP, MNp-CS and MNp-CO were found as 1.86, 2.79 and 1.30 mg g-1 respectively.

Kamath et al. (2020) synthesized iron oxide nanoparticles showed a high affinity toward As (V) adsorption, although the oakleaf FeNP and eucalyptus leaf (EL) FeNP showed particularly higher adsorption capacity than green tea, black tea, and pomegranate leaf FeNP. EL-FeNP was determined to be having the highest adsorption capacity of 39.84 mg g-1, followed by oakleaf FeNP of 32.05 mg g-1. Eucalyptus and oakleafs extracts were most suitable candidates for the preparation of iron oxide nanoparticles for arsenic adsorption.

The kinetic studies show that high efficiency of magnetic Fe-hydrotalcite (M FeHT) produced by a coprecipitation method for arsenic adsorption can be achieved approximately 95% adsorption of As(V) and As(III) was achieved within the first 15 min of contact (Türk and Alp 2014). In experimental studies, 500 mg adsorbent was added into 100 mL of As(V) solution in a 100 mL flask. In our experiment, we used only 1 mg of nanoabsorbent (Fe3O4NPs, Fe3O4 GONCs, Fe3O4GOEDTA NCs, and Fe3O4GOGlutat NCs) in each 50 mL flasks to remove the aqueous arsenic during 24 hours. Comparing the MFeHT (500 mg) performance we succeded satisfactory absorbance (81.39% arsenic removal) with a lower amount of nanoadsorbent. These results will be important for the remediation processes that prefer to use lower amount nanoadsorbent in higher volume of water due to aquatic conservation concerns. Also, in the current study, batch experiments were conducted by using the normal tap water and pH levels of the water was not modified more reflecting practical remediation programs.

Lin et al. (2022) produced the calcined green synthesized Fe/Ni nanoparticles (C–Fe/Ni NPs) and evaluated for their efficacy for As (V) adsorption from aqueous solution. As (V) adsorption efficiency reached 87.3% under experimental conditions. The decrease in adsorption efficiency for an increasing of initial As (V) concentration could be resulted from the limited number of active adsorption sites existed for a fixed dose of the material. Moreover, in this study, it was stated that adsorption efficiency was very low at relatively low As concentrations (0.5 and 1.0 mg L-1) because of the collision probability with the surface was smaller at low pollutant concentrations. In our study, the maximum adsorbance was obtained from Fe3O4NPs treatment with the adsorbance value of 81.39%. Considering the current adsorbance value and the initial concentration of As (0.088 mg L-1), it could be stated that the present study was quite succecfull.

Graphene oxide (GO) can be used effectively in wastewater remediation processes due to its high surface area as well as the functional groups on its surface. Removal of heavy metal ions by adsorption occurs through complexation with the oxide binding site in graphene. In a study conducted by Wu et al. (2018) used graphene oxide (GO)-based adsorbent (GO/CuFe2O4) to remove both As(III) and As(V). The maximum adsorption capacities (mg g-1) achieved were 51.64 for As(III) and 124.69 for As (V). Both As(III) and As(V) adsorptions on GO-CuFe2O4 adsorbent followed an inner sphere complex mechanism. In another study conducted by Su et al. (2017), a modified iron oxide-graphene oxide NCs were used to remove 99.9% of both As(III) and As(V) successfully. The maximum adsorption capacities were 147 mg g-1 for As(III) and 113 mg g-1 for As(V). These investigations showed that the adsorption processes of As onto modified-GO takes place through a mechanism known as surface complexation. GO is characterized by diverse functional groups on its surface, including epoxy, lactol, carboxyl, phenol, and hydroxyl groups, along with large π-stacking. These features enable GO to possess a high adsorption capacity through strong interactions such as hydrogen bonding, electrostatic forces, and π-π interactions (Gabris et al. 2022). But, in our study, all GO NCs (Fe3O4 GONCs, Fe3O4GOEDTA NCs, and Fe3O4GOGlutat NCs) showed lower As adsorbance performances compared to bare Fe3O4NPs. These unpredicted results might be caused from irregular surface complexation, capping of the surface, the lower DLS and zeta potentials of GO NCs. Also, in the current study, the best adsorption of aqueous arsenic was achived by 12-86 nm sized IONPs synthesized in ethylene glikol (Figure 1, Table 1). Although Fe3O4GO NCs had the similar size (13-32 nm) with Fe3O4 NPs (12-86 nm), the adsorbance capacity of GO NCs (70.45%) was lower than that of IONPs (81.39%). This situation may be attributed to the surface characteristics (lower zeta potential of NCs (-10.4 versus -15.3 mV) and FTIR spectrums) of the NPs and NCs. It has well known that various adsorption forces such as electrostatic interactions, ion exchange and ion association tendencies, and complex formations play an important role in the arsenic adsorption mechanism on the surfaces of oxide forms of iron (Polowczyk et al. 2018).

Arsenic concentrations in drinking water have been reported as high as 1.320 µg/L (Nicaragua), while groundwater and wastewater levels exceeded 5.000 µg/L (Thailand) and 134.000 µg/L (landfill leachate in Brazil), respectively. Moreover, bioaccumulations of arsenic in fish species ranges from 0.4 (catfish in the Paraná River Delta, Brazil) to 362µg/g (Pteromylaeus bovinus, Northern Adriatic Sea). Although it is commonly known that inorganic As (iAs) is typically more toxic than organo arsenic species, the toxicity of iAs species toward marine organisms is still a topic of debate (Rahman et al. 2012). Marine phytoplankton show higher sensitivity to arsenite (AsIII), while freshwater phytoplankton are highly sensitive to arsenate (AsV) (Mojiri et al. 2024).

Although many investigations have been conducted on arsenic toxicity in aquatic organisms, there is no record on bioaccumulation of the heavy metals in freshwater medicinal leech, Hirudo verbana. At the end of the biocompability tests; the concentrations of Mn, Fe, Co, Zn, As and Hg increased, while, Al, Cu and Pb concentrations decreased in H verbana tissues with the different doses of Fe3O4 NPs significantly. This situation could be attributed to the fact that iron nanoparticles's adsorption of the these heavy metals and acceleration of their passages to the leech tissues through nanostructures. In particular, it can be declared from the current results that As, Fe, Mn, Co accumulations in leech tissues reflect the effective adsortion of both As, Mn, Fe and Co by Fe3O4 NPs. Because this study was the first report investigating the effects on bio-accumulations of heavy metals in medicinal leeches (H verbana) exposed to NPs in the literature, the current data could not compared with the other studies. Also, there was no mortality detected in all experimental groups exposed to different doses of Fe3O4 NPs (survival rates were 100% in all groups).

On the other hand, the advancement in technology with the use of nanoparticles for As remediation also comes with toxic effects that can be hazardous for humans, animals, plants and the environment. NPs are the major factors due to which they can easily access the internal organs and tissues, and can subsequently accumulate in humans and animals' tissues. Toxicity of NPs in aquatic environment depends on their nature, reactivity, exposure concentration, shape, size, solubilizing, agglomerating characteristics, surface charge as well as time of exposure, medium composition, route of particle administration and target species (Jastrzębska and Olszyna 2015; Manuja et al. 2021). In particular, mussels decreased their metabolic capacity, reduced energy expenditure, increased oxidative stress and lipid damage when exposed to NPs (Huang et al. 2018; Freitas et al. 2018). In addition, Au-NPs and cadmium chloride (CdCl2) caused the highest oxidative stress and cellular damage in M. edulis (Tedesco et al. 2010). CuNPs are deposited in gills and can caused oxidative stress in crayfish exposed to NPs for a long time (Yang et al. 2022).

Nguyen et al. (2020) determined a significant decrease in copper toxicity by using Fe-Cu bimetallic oxide nanoparticles (500 µg/mL) for the treatment of rat kidney proximal tubule epithelial cells (NRK-52E). While the control group (CuO) shows a great decrement in survival rate (8%), Fe-Cu bimetallic oxide nanoparticles treated NRK-52E cell line had about 94% survival, whereas approximately 100% survival rate was detected for Fe3O4 nanoparticles on the same cell lines using similar concentrations. In another study conducted by Maity et al. (2009) stated that magnetite nanoparticles (Fe3O4 NPs) were biocompatible up to the iron concentration of 80 µg ml-1 with SiHa, B16F10 and mouse primary fibroblast cells. These findings were very similar to the current results which observed 100% survival in all experimental groups of medicinal leeches exposed to different doses of Fe3O4 NPs. Both two results clearly showed that Fe3O4 NPs and Fe-Cu-NPs are not cytotoxic and can also greatly reduce the copper and arsenic toxicities through the adsorption processes.

In conclusion, Fe3O4 NPs had the highest As adsorbance capacity comparing with GO, GO-EDTA, and GO-GLU NCs in freshwater adsorption experiments. Also, Fe3O4 NPs had no toxicity effect on the medicinal leeches H verbana with respect to survival and biocompability. In future perspectives, it can be advised to use Fe3O4 NPs in city wastewater remediation plants and develop the similar processes by using these NPs to their good characteristics such as higher As adsorbance and biocompability for the sustainable environmental conservation.

Ethical statement

Ethics approval and consent to participate not applicable for this study.

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Author Contributions

First author: conceptualization, data curation, writing original draft, project administration; Second author: formal analysis, methodology, Third author: visualization, supervision, review and editing

Conflict of Interest

The authors declare that they have no known competing financial or non-financial, professional, or personal conflicts that could have appeared to influence the work reported in this paper.

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