Remediation of arsenic contaminated groundwater with magnetite (Fe₃O₄) and chitosan coated Fe₃O₄ nanoparticles

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ABSTRACT: Nanoparticles, due to their high surface area, regenerative properties and possibility of in situ treatment, exhibited their application potential in capturing arsenic (As). The objective of the current study is to explore the potential of As adsorption by Fe₃O₄ nanoparticles (IONPs) and Chitosan coated Fe₃O₄ nanoparticles (Ch-IONPs). Batch experiments performed with an initial As(III) and As(V) concentration of 0.125 mg L⁻¹, revealed a maximum As removal of 99.9% in 0.4 g L⁻¹ IONPs and 0.6 g L⁻¹ Ch-IONPs, at a pH equal to 7.0 and room temperature. The maximum adsorption capacity of IONPs and Ch-IONPs was 213.25 and 118.67 µg g⁻¹ for As(III) and 239.50 and 116.33 µg g⁻¹ for As(V), respectively. The Pearson Correlation value showed a better correlation with Freundlich isotherm (R² = 0.96) than Langmuir isotherm (R² = 0.87). The results of this work suggest that the incorporation of IONPs and Ch-IONPs as adsorbents, offer a promising option for As removal in water treatment.

1 INTRODUCTION

Arsenic (As) contamination in groundwater is a major global health concern. Arsenite [As(III)] is supposed to be 60 times more poisonous and mobile than arsenate [As(V)] (De *et al.*, 2009). Among various technologies already in use for removal of As from contaminated groundwater, namely coagulation, filtration, membrane separation and ion exchange; adsorption offers many advantages like ease of operation, simple waste handling and low operation cost. Magnetite (Fe₃O₄) nanoparticles exhibit excellent magnetic properties, which are being investigated for their application in water purification for the removal of heavy metals, such as lead and As (Feng *et al.*, 2012; Mayo *et al.*, 2007). The surface of these nanoparticles can be revamped according to desired functionalities, by methods like coating with surfactants or polymers. The aim of the current study is to find out the optimum conditions for the removal of As(III) and As(V) species by laboratory-synthesized Fe₃O₄ nanoparticles (IONPs) and chitosan coated Fe₃O₄ nanoparticles (Ch-IONPs). The removal capacity was studied by applying batch experiments and inferred by isotherm study.

2 MATERIALS AND METHODS

2.1 Synthesis of IONPs and Ch-IONPs

For the synthesis of IONPs by co-precipitation, 10 mg FeCl₃·6H₂O was dissolved in 200 mL distilled water. To this, 4 mg FeSO₄·7H₂O was added, and the mixture heated to 55°C for 10 min. NH₄OH was rapidly added to the heated mixture for maintaining pH at 10. The final solution was centrifuged, washed with distilled water and ethanol, finally oven dried for 12 hours. For the Ch-IONPs' synthesis, 5 mg FeCl₃·6H₂O

was mixed with 2 mg FeCl₂·4H₂O in 100 mL distilled water. Chitosan, 0.2 mg, was added in a 20 mL mixture of 1 mL acetic acid (2N) and 19 mL distilled water. Both the above mixtures were then mixed and pH was adjusted to 6.9. NH₄OH was then added after passing dry N₂ gas at 80°C. The final solution was centrifuged, washed with distilled water and ethanol, finally oven dried for 12 h.

2.2 Effect of pH and adsorbent dose on As(III) and As(V) removal

To study the effect of pH on As adsorption behavior of IONPs and Ch-IONPs, 50 mg of each of IONPs and Ch-IONPs were added in 50 mL NaAsO₂ solution (0.125 mg L⁻¹) and 50 mL NaHASO₄ solution (0.125 mg L⁻¹), respectively. Batch study for IONPs and Ch-IONPs was performed by adjusting the pH at 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 in different batches (shaken for 60 minutes), adding 0.01 M HCl or 0.1 M NaOH. The study suggested an optimum pH of 7.0, which was kept constant and the dosage of IONPs and Ch-IONPs was varied, i.e. 5, 10, 15, 20, 30, 40 and 50 mg in each batch of 50 mL NaAsO₂ solution and 50 mL NaHASO₄ solution, respectively, to optimize the adsorbent dose for As(III) and As(V) adsorption and shaken for 60 min.

3 RESULTS AND DISCUSSION

3.1 Characterization of IONPs

The morphology of IONPs was studied using Field Emission Scanning Electron Microscope (FESEM), which confirms the formation of peanut shaped IONPs with an average size of 30 to 80 nm. The FESEM images of IONPs and Ch-IONPs are shown in

Figure 1. (a) FESEM image of IONPs with particle size (b) FESEM image of Ch-IONPs (c) XRD analysis image of IONPs.

Table 1. Effect of pH on As(III) and As(V) adsorption onto IONPs and Ch-IONPs, % removal values.

pH	As(III)		As(V)	
	IONP	Ch-IONP	IONP	Ch-IONP
4.0	66.92	82.40	86.72	45.92
5.0	99.90	87.84	89.28	88.36
6.0	99.90	93.92	99.80	95.48
7.0	99.90	99.90	99.90	97.84
8.0	99.90	87.80	99.90	85.40
9.0	99.90	76.96	94.68	79.64

Figure 1(a) and (b), respectively. The X-ray diffraction (XRD) analysis confirmed the existence of IONPs and Ch-IONPs by showing clear peaks at diffraction angles of 35.246, 42.831, 53.128 and 74.530 (Okudera *et al.*, 1996). The XRD image of the formed IONPs is shown in Figure 1(c).

3.2 Batch studies for As(III) and As(V) removal

A maximum As(III) and As(V) removal capacity of 99.9% was achieved at an initial concentration of 0.125 mg L⁻¹ As(III) and As(V), at pH equal to 7.0, which can be attributed to the fact that metal ions get easily adsorbed due to the protonated surface amine groups. Table 1 summarizes the results of pH study. The critical dose for As(III) and As(V) adsorption was observed as 0.4 g L⁻¹ for IONPs and 0.6 g L⁻¹ Ch-IONPs. A rapid increase in % As removal with an increase in the adsorbent dose of IONPs and Ch-IONPs (5.0 mg to 50.0 mg, in 50 ml solution) was observed. This is due to the increase in available adsorption sites on the surface of the adsorbent. Table 2 summarizes the results of adsorbent dose study.

3.3 As(III) and As(V) adsorption isotherm

The isotherm studies reveal the maximum adsorption capacity of IONPs equal to 213.25 μg g⁻¹ for As(III) and 239.50 μg g⁻¹ for As(V). A decrease of adsorption capacity in case of Ch-IONPs to 118.67 μg g⁻¹ for As(III) and 116.33 μg g⁻¹ for As(V) was observed. This can be explained by Chitosan's coating on the adsorption sites available on virgin IONPs, which

Table 2. Effect of adsorbent dose on As(III) and As(V) adsorption onto IONPs and Ch-IONPs, % removal values.

Adsorbent Dose (mg)	As(III)		As(V)	
	IONP	Ch-IONP	IONP	Ch-IONP
5.0	65.00	47.64	79	60.32
10.0	75.40	59.16	87.90	72.16
15.0	77.20	86.24	88.40	75.12
20.0	99.90	99.90	88.08	99.90
30.0	99.90	99.90	99.90	99.90
40.0	99.90	99.90	99.90	99.90
50.0	99.90	99.90	99.90	99.90

reduces the removal capacity of Ch-IONPs. The Pearson Correlation value showed a better correlation with Freundlich isotherm ($R^2 = 0.96$) than Langmuir isotherm ($R^2 = 0.87$).

4 CONCLUSIONS

Considering the average As concentration (~100 μg L⁻¹) in the Brahmaputra flood plain (as per literature reviewed), maximum As removal was achieved at a dose of 0.4 g L⁻¹ for IONPs and 0.6 g L⁻¹ for Ch-IONPs. As(V) removal was observed to be 20% (approx.) higher than As(III) removal, both for IONPs and Ch-IONPs. Further, the results also showed that the removal efficiency of IONPs was 1.5 times more than Ch-IONPs'. Both these nanomaterials can be locally (in house) used for a low As concentration as well as for a higher As concentration. Also, IONPs and Ch-IONPs used in this adsorption process can be separated easily with a magnet, washed and their surface can be regenerated for reuse.

ACKNOWLEDGEMENTS

Authors sincerely thank the Department of Civil Engineering, IIT Guwahati for providing the lab facilities and chemicals. Authors also acknowledge the Central Instruments Facility, IIT Guwahati for FESEM and XRD analysis.

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Removal of arsenic from wastewater treated by means of nanoparticles and magnetic separation

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ABSTRACT: This work is carried out based on the importance of the enormous consumption of water, which is obliged to comply with current regulations for the use to which it is intended. Because the arsenic is a toxic element and exposure to it, even in small amounts, can cause serious health problems, the water supplied to the services must comply with the maximum permissible limits. Therefore, it will use two iron oxide nanoparticles that allow the elimination of said pollutant and, in turn, the nanoparticles will be recovered through the application of a magnetic field for its regeneration and subsequent reuse, determining its life cycle. By establishing the optimal adsorption conditions for each of the nanoparticles, the removal of arsenic in a contact device water – nanoparticles – magnetic field using only the most efficient nanoparticles and the use wastewater treated real will be carried out.

1 INTRODUCTION

Arsenic (As) is a natural element from earth's crust; widely distributed through all the environment. Ingestion of small amounts of As can cause chronic effects due to its bioaccumulation in the organism. Prolonged exposure to inorganic As, through the consumption of contaminated water or food prepared with it and food crops watered with As-rich water can cause chronic intoxication.

The treatment train that municipal wastewater in Mexico receives includes physical, chemical and biological processes generally, under the operating conditions in which these processes are realized, certain pollutants, such as heavy metals, are not removed (Abejón & Garea, 2015).

Nanoparticles (NPs) are materials with a nanometric size on its three dimensions; as a result of its small size, they possess structural and morphological characteristics which make them ideal for some kind of applications. Specifically, magnetic NPs are efficient for As polluted water treatment up to the grade of obtaining water suitable for human consumption, sanitizing and irrigation. Due to the big use of superficies in proportion to its volume and they link easily to chemical substances, they can be eliminated, applying a magnetic field (Liyun *et al.*, 2012; Yavuz *et al.*, 2006).

Magnetic NPs base on iron, both magnetic and oxidized iron offer stronger magnetic susceptibility, high chemical stability, and low toxicity, so its use on water treatment results efficient, obtaining water with As concentrations under maximum level permissions established by Mexican Official Norms (NOM-127-SSA1-1994).

Table 1. NPs to use.

NPs	Description	Physical appearance
Iron oxide (Fe ₂ O ₃)	Magnetic and semiconductor NPs	Fine reddish powder without characteristid aroma
Graphene functionalized with Fe ₂ O ₃	Graphene microflake reduced and functionalized with Fe ₂ O ₃ (2% a 5%)	Black pasta

2 METHODOLOGY

2.1 Selection of parameters

This first stage will be carried out using commercial iron oxide NPs (Table 1), model solutions of wastewater treated with known concentrations of As was prepared.

The optimal work parameters will be established: concentration As-dose NPs, pH, temperature, agitation and contact time. In order to identify which of the NPs has a greater capacity for removing As kinetics and isotherms of adsorption will be carried out with each of them.

2.2 Design of contact device

Once the working parameters have been optimized and NPs have been identified that allow for greater elimination of As, a prototype device at laboratory scale