Chapter 10
Iron Oxide Nanoparticles to Remove Arsenic from Water

Prabhat Parida, Mayura Lolage, Ashwini Angal, and Debabrata Rautaray

Abstract Arsenic contamination in water is a widespread problem globally. Millions of people depend on arsenic-contaminated groundwater. Arsenic poisoning leads to fatal diseases such as skin and internal cancers. Hence, the current regulation of drinking water standard has become more stringent and requires arsenic content to be reduced to a few parts per billion. Therefore, effective and inexpensive technologies for arsenic removal are needed. Majority of communities affected by arsenic contamination could not justify the cost and maintenance of installing centralized arsenic treatment systems. Thus, there is a need to develop point-of-use water treatment devices. Here we review arsenic contamination, it's health effects, and available removal technologies. We then describe the development of a working prototype cartridge to remove arsenic from drinking water that meets international standard norms. For that we synthesized iron oxide nanoparticles using a chitosan biopolymer. Iron oxide originated from steel waste. Granules were thereafter packed in a column and evaluated for arsenic removal efficiency using simulated ground water compositions.

Keywords Arsenic • Arsenic removal technologies • Arsenic adsorption • Arsenic remediation • Water purification • Iron oxide • Drinking water • Point-of-use water treatment • Ground water contamination • Arsenic toxicology

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10.1 Introduction

Arsenic in drinking water is a major problem and the health effects have been observed in populations drinking arsenic-rich water over long periods of time in countries world-wide (Smith et al. 2000). Long-term exposure to arsenic via drinking-water causes cancer of the skin, lungs, urinary bladder and kidney infections. The toxic and carcinogenic effects of arsenic on living beings are well documented (Tchounwou et al. 2003). Arsenic is an odourless, colourless and tasteless semi metallic element, which is a naturally occurring element in the environment. Arsenic is introduced in the drinking water sources through geochemical reactions, industrial waste discharges, or agricultural use of arsenical pesticides.

Arsenic in soil or ground water is usually present either in the form of arsenite with +3 charges, or arsenate with a + 5 charges. Both arsenate (As–V) and arsenite (As–III) tend to combine with multiple oxygen atoms, each having −2 charges. Arsenite and arsenate compound in dissolved form tend to have an overall negative charge. Arsenite exists under anaerobic conditions, for example in water-logged soils. Under more oxidizing conditions, arsenite converts to arsenate. Arsenate naturally sorbs to soil minerals, particularly iron oxides and hydroxides. Arsenite tends to sorb less strongly than arsenate (Spayd et al. 2012). Arsenate is most common in surface waters while arsenite is more common in ground waters (Oremland and Stolz 2005). Arsenite is 10–60 times more toxic than arsenate. Concentrations of arsenite are particularly significant from a human health perspective, although arsenic levels are typically reported as total arsenic (Vu et al. 2003).

10.1.1 Arsenic Contamination of Ground Water

Groundwater resources have been the main source of exposure for millions of people in developing nations to high levels of inorganic arsenic (Nickson et al. 1998; Shankar et al. 2014). Although arsenic levels in natural waters do not usually exceed several parts per billion (ppb), drinking water in many regions of the world contain concentrations of total arsenic in excess of 100 ppb. World health organization (WHO) and U.S. environmental protection agency (USEPA) have recently revised the maximum contaminant level in drinking from 50 ppb to 10 ppb. If other safe water sources are unavailable, removal technologies are usually applied to lower arsenic concentration to the prevailing regulatory standard or to a level that poses the minimal threat to human health (Jadhav et al. 2015).

Arsenic contamination of drinking water poses a much greater challenge for developing nations. This is because water treatment required for arsenic mitigation often involves technologies that are relatively complex and costly. This problem is intensified in rural areas where access to safe drinking water is already limited. Arsenic being colourless and odourless poses a problem for rural communities with a perception that water is clean when it does not have any visible contaminants

(Smith et al. 2000). Another contributing factor to the large arsenic contamination problem for developing nations is the lack of proper nutrition. Those communities that are excessively poor and malnourished tend to experience more symptoms of arsenic poisoning such as arsenicosis and are more susceptible to develop chronic internal cancers (Saha et al. 1999).

10.1.2 Health Effect due to Exposure to Arsenic

Inorganic arsenic is considered the most potential human carcinogen and humans are exposed to it from soil, water, air and food. Chronic toxicity is observed from exposure to drinking water that contains ppb levels of inorganic arsenic. Acute poisoning has many metabolic effects, including stomach pain, diarrhoea, vomiting, bloody urine, anuria, shock, convulsions, coma and death (Singh et al. 2015). The consequences of exposure to arsenic for human health are potentially grave and may extend from general malaise to death. Chronic and systemic exposure to arsenic can lead to serious disorders, such as vascular diseases (black foot disease and hypertension) and irritations of the skin and mucous membranes as well as dermatitis, keratosis, and melanosis. The clinical manifestations of chronic arsenic intoxication are referred to as arsenicosis (hyperpigmentation and keratosis). It is, therefore, important to measure the arsenic levels in water resources (i.e. groundwater and surface water), in order to identify potential problems before they give rise to adverse health effects within the population (Sharma and Sohn 2009). Additional health effect of arsenic includes cancer of the bladder, lungs, skin, kidney, liver, prostrate and nasal passage (Yoshida et al. 2004 and Saha et al. 1999). Arsenic also harms the central and peripheral nervous systems and causes several skin disorders. Absorption of arsenic through the skin is minimal; therefore, hand washing or bathing with arsenic contaminated water does not pose human health risks.

10.1.3 Arsenic Removal Technologies

There are currently no simple and inexpensive effective technologies to mitigate such problems and as a result, arsenic mitigation approaches vary greatly from large, developed cities served by centralized water supplies to small rural communities in developing nations. There are number of arsenic removal methods that are suitable for the treatment of drinking water including anion exchange resins, porous ceramics, activated alumina and iron flocculation processes (Mohan and Pittman 2007 and Ramos et al. 2014 and Zaspalis et al. 2007). Conventional polymeric anion exchangers have a low selectivity for arsenate and at the same time the high concentration of sulfate in drinking water successfully competes with arsenate for available anion exchange sites resulting in a short operational life (Meng et al. 2000). While on the other hand, coagulation using iron flocculants as a treatment method is highly effective in removing arsenic from water but generates large amounts of a ferric hydroxide flocculants which will require safe disposal in a landfill. Therefore, capital equipment requirements are generally high (Vaclavikova et al. 2008 and Tara et al. 2013).

Among various agents used in the purification and treatment of arsenic rich water, iron-based materials have gathered specific attention in view of their special qualities such as their earth-abundant and environmentally friendly nature (Thomas 2015). Water treatment method involving the use of low cost natural iron oxide minerals such as laterite for arsenic removal to meet drinking water standards has been well documented in the literature (Aredes et al. 2012). Various studies revealed that arsenate adsorption is related to the iron content of adsorbents, and adsorption rate increases in the following order: goethite < hematite < magnetite < zero valent iron (Pajany et al. 2011). It is also shown through desorption experiment; arsenic is strongly adsorbed onto hematite and zero valent iron. Among adsorbents, hematite appears to be better for removing arsenate in natural medium since it is effective over large ranges of pH and arsenic concentration (Pajany et al. 2009, 2011 and Grafe et al. 2001). Liu et al. have prepared iron oxide impregnated chitosan bead(s) using reverse phase suspension method to remove As (III) from water (Liu et al. 2010). Jiang et al. have shown chitosan-coated sand and iron–chitosan-coated sand for the removal of both As (V) and As (III) from aqueous systems. Various parameters including pH, equilibration time, initial arsenic concentration and adsorbent dosage have been optimized for maximum adsorption of arsenic (Jiang et al. 2013). Oxidation of As (III) to As (V) is also needed for effective removal of arsenic from groundwater by most treatment methods. Thus there is a need for a water purification composition which is effective in removing both arsenic species [As (V) and As (III)] from water. Additionally, the cost effectiveness of the arsenic purification system and safe disposal of the spent media are extremely important.

10.1.4 Use of Nanotechnology for Arsenic Removal

Properties of nanoparticles are exploited in fields such as catalysis, separation, sensor, biological, molecular isolation, chemical and physical adsorption applications. Recently nanoparticles are being increasingly used in adsorption processes for water purification as well mainly due to their available active high surface area and unusual unique properties. For example, both As (V) and As (III) can strongly adsorb onto metal oxide nanoparticles with high sorption capacities. A number of reports have shown that nano-sized sorbents such as elemental iron, titanium oxide and iron oxide are more effective compared to macro-sized particles (Mostafa and Hoinkis 2012). The high surface area to mass ratio, high surface reactivity and unique catalytic activity are the most important properties of a nanomaterial and led to increased efficiency as an adsorbent compare to macro-sized of the material. Nanoparticles of metal oxides such as Fe_2O_3, Fe_3O_4, TiO_2, Al_2O_3 etc. among others are promising for their large surface area and porous structure and have been used in water and wastewater purification processes as adsorbents (Mostafa and Hoinkis 2012).

Other nanostructures such as three-dimensional graphene-carbon nanotube-iron oxide nanostructures have been shown for absorption for arsenic from contaminated water, due to its high surface-to-volume ratio and the open pore network of graphene-carbon nanotube-iron oxide 3D nanostructures (Vadahanambi et al. 2013). CuO nanoparticles are shown to have effectively removing arsenic from groundwater. It was shown effectively removed both As (III) and As (V) between pH 6 and 10. In this study, the presence of sulfate and silicate in water did not inhibit adsorption of As (V) but only slightly inhibited adsorption of As (III) (Martinson and Reddy 2009). Multi-walled boron nitride nanotubes functionalized with Fe_3O_4 nanoparticles were also used for arsenic removal from water. The magnetite nanoparticles functionalized on multiwall boron nitride nanotubes led to a simple and rapid separation of magnetic metal-loaded adsorbents from the treated water under an external magnetic field (Chena et al. 2011).The Fe–Cu binary nano-oxide could also be a promising adsorbent for both As (V) and As (III) removal because of its excellent performance, facile and low-cost synthesis process, and easy regeneration (Zhanga et al. 2013). Magnetic nanoparticles modified simultaneously with amorphous Fe and Mn oxides were shown also to remove arsenite from water (Shan and Tong 2013).

10.1.5 Advantages of Nanostructured Iron Oxide for Arsenic Removal

Nanostructured iron oxide adsorbent used for the removal of arsenic uses the combined catalytic and adsorptive properties of iron oxide to breakdown arsenic into less toxic by-products while facilitating the filtration of these by-products out of the groundwater (Sylvester et al. 2007 and Mayo et al. 2007). Nanophase Fe_3O_4 and Fe_2O_3 were synthesized through precipitation method and were utilized for the removal of either arsenic (III) or (V) from aqueous solution as a possible method for drinking water treatment (Luther et al. 2012; Sharma et al. 2015). Alpha-Fe_2O_3 nanowires deposited onto diatomite was shown to remove efficiently As (III) and As (V). Parameters, such as adsorbent quantity, adsorption time, adsorption temperature, pH value, and initial As (III) or As (V) concentration, was shown to influence the As (III) or As (V) removal efficiency of the alpha Fe_2O_3 nanowires/diatomite sample (Du et al. 2013). Super paramagnetic iron oxide nanoparticles surface-coated with 3-mercaptopropanoic acid having an attribute of increased active adsorption sites were shown to remove arsenate from drinking water (Morilloa et al. 2015). Polymeric beads containing hydrous iron oxide nanoparticles (25% dry weight) was shown to effectively remove As (III) (Gang et al. 2010 and Katsoyiannis and Zouboulis 2003). Abid et al. have demonstrated iron oxide nanoparticles synthesized in large scale through gas-phase diffusion flame synthesis having smaller particle diameter and large surface area. These flame synthesised iron oxide nanoparticles has been shown significantly effective in removal of As (V) from water. Furthermore, the author have shown that by controlling Fe(III)/Fe(II) ratio, the arsenic adsorption capacity can be increased multi-fold (Abid et al. 2013). Liu et al. have explained the probable mechanism that involves in the adsorption of arsenic onto iron oxide. As (III) and As (V) both form bidentate, bimolecular surface complexes with FeOH (or FeOOH or hydrous ferric oxide), as the primary species tightly immobilized on the iron surface. As (V) oxyanions (chemical moiety) are attracted to the iron-oxide-coated surfaces and bound with the active sites (A-OH groups), through weak intermolecular hydrogen bonding. Finally they are bound with the surfaces, eliminating water molecules (Maji et al. 2012). The primary factor make iron based adsorptive media treatment is attractive due to the fact that the system is low-cost and simple to operate. The affinity of iron media for arsenic is strong under natural pH conditions (Maji et al. 2012). This feature allows iron based sorbents to treat more bed volumes without the need for pH adjustment. Iron oxide (nano) systems are known to provide long operating cycles and low operating costs. Life expectancy is dependent on site-specific water quality and operating levels. Exhausted media is non-hazardous and can be disposed of using conventional methods.

10.1.6 Point of Use Water Purification

Point of use water purification devices are appropriate for removing contaminants that pose only an ingestion risk, as is the case with arsenic. Since only a small fraction of the total water supplied to a given household is ultimately treated and consumed, only that small fraction (the water intended solely for consumption-drinking and cooking) needs to be treated in order to reduce the risk. The primary advantage of using point of use treatment in a small system is a reduction in capital and treatment costs, relative to installing centralized treatment. Here, we demonstrate a working prototype cartridge that removes arsenic from water (without any side effects such as leaching) that meets appropriate standard protocols. In order to achieve this, we have used iron oxide nano powders obtained from a waste generated from a steel manufacturing plant. We have evaluated iron oxide fine powder for their chemical and physical properties, formulated an efficient composition, worked on a form-factor, customized a testing protocol plan against arsenic and studied the arsenic removal efficacy over a life 1000 l of water.

10.2 Experimental Section

The source of iron oxide fine powders used for the purpose of arsenic removal is obtained from a steel manufacturing plant (where it is generated as a waste), which also poses disposal problem in an eco-friendly manner. The iron oxide powder was thoroughly characterized using various techniques such as X-ray fluorescence (XRF) spectroscopy for compositional analysis, X-ray diffraction (XRD) for crystal structure determination, thermo gravimetric analysis (TGA) for quantification, Brunauer–Emmett–Teller (BET) for surface area measurement, particle size measurement through dynamic light scattering method (PSD), Zeta potential for surface charge estimation and scanning electron microscopy (SEM) for particle size and morphology studies.

10.2.1 Formulation: Preparation of Granule of Chitosan Coated Iron Oxide Particles

About 500 g of citric acid is dissolved in 10 l of distilled water by stirring for 15 min in a vessel to obtain a solution. 200 g of chitosan is added to above solution under constant stirring for 1 h to facilitate mixing of chitosan thoroughly in the solution. 2000 g of iron oxide fine powder is added slowly under stirring to the solution obtained from the previous step followed by stirring for 1 h to facilitate mixing of iron oxide particles properly. 2 l of 10% (w/v) sodium hydroxide solution is added to the solution obtained from the previous step to facilitate precipitation of iron-chitosan matrix with the help of a master flex pump, such that the rate of addition of sodium hydroxide is 100 ml/min. Addition of sodium hydroxide solution is followed by stirring for 1 h. After said stirring, the contents of the vessel are transferred to a beaker of 10 l capacity. The precipitate is allowed to settle down. Separate the precipitate by decanting water from the beaker. The precipitate is then washed by adding 2 l of distilled water to the beaker followed by stirring for 5 min. The precipitate is then allowed to settle down and separated from the beaker again by decanting water from the beaker. The precipitate is washed again by repeating the step of washing. After washing the precipitate twice, the precipitate is transferred to a drying tray for drying at a temperature of 90–100 °C. Drying is carried out in a drying oven. The precipitate is removed from the oven while having 20–25% of moisture. This is then subjected to mild grinding to facilitate breaking of lumps followed by further drying at a temperature of 90–100 °C. The dried precipitate thus obtained is subjected to sieving through a nylon net having pore size of approximately 1 mm. The precipitate remaining on the top of the net is milled to facilitate breaking. The dried precipitate which passes through the net is collected and sieved through a mesh of pore size 150 μm to obtain granules. The granules are collected on the top of the mesh. The granules have a size in the range of 0.15–1 mm.

10.2.2 Prototype Designing to House Iron Oxide Granules for Arsenic Removal from Water

Iron oxide granules are accommodated in a cylindrical column with a screen at the bottom to protect iron fine leaching (Fig. 10.1). Appropriate flow rate is maintained using a knob attached outside the column. Photograph below illustrates the details

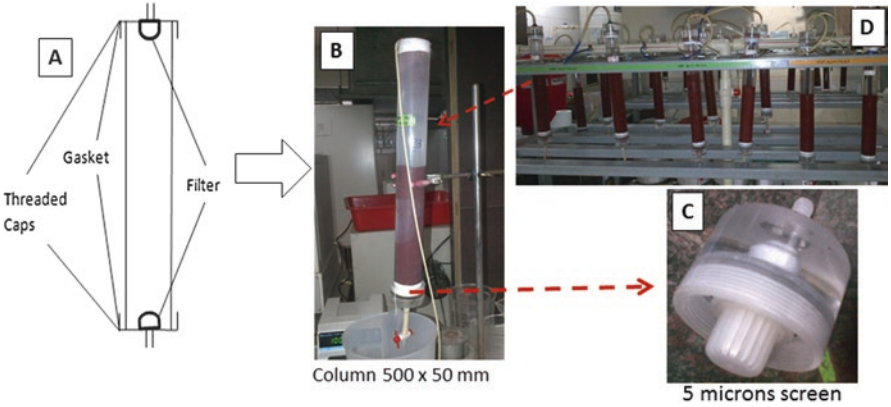

Fig. 10.1 (**a**) Basic drawing of the fabricated column; (**b**) Photograph of a cylindrical column packed with Iron oxide granules; (**c**) Photograph of a specially designed screen of 5 microns to restrict iron oxide leaching; and (**d**) Photograph of a water testing platform to evaluate performance of arsenic removal filters

of the column fabricated to house the iron oxide granules. The cylindrical column used is 500 mm in height and 50 mm in diameter and is fabricated with a distinctively designed screen of pore size ~5 microns. The screen is designed in a manner that restricts granules or iron fines to escape into the output water. The special design of the screen also helps overcoming any choking of the filter over its life. The columns are packed with 200 g of iron oxide granules containing granule size ranging 150 microns to 1 mm size.

Once granules are packed, approximately ~4 l of reverse osmosis (RO) water is passed through the granules to remove fine particles of iron oxide (if any) that passes through the screen. Washing is continued until clear water is obtained in the output water. Thereafter, washed packed columns are installed in the testing lines (Fig. 10.1d) to conduct trials as per standard testing protocols.

10.2.3 Evaluation Protocol for Arsenic Removal from Water: Guidelines for Water Purifier Against Arsenic (III and V –Influent and Effluent)

Based on our studies of various protocols [NSF/ANSI 53–2011, US-EPA and BIS –IS3025 (Part 37)], we have designed a simulated ground water conditions for input challenge water for spiking and quality assurance of output water. US-EPA and NSF have marginally different protocols for arsenic. However, NSF international body has prepared the US-EPA protocol for arsenic removal from water. NSF has also created a separate protocol for point of use unit for arsenic removal. Both the protocols says different ways of treating Arsenic III and Arsenic V species, however the

Table 10.1 Composition of input challenge test water for 50 ppb arsenic (III)

Source	Parameter	Addition of salt (mg/l)
Sodium silicate ($Na_2SiO_3.9H_2O$)	(silica) 20 mg/l	93 mg/l
Sodium nitrate ($NaNO_3$)	(Nitrate) 2.0 mg/l	12 mg/l
Magnesium sulphate ($MgSO_4.7H_2O$)	(magnesium) 12 mg/l	128 mg/l
Sodium fluoride (NaF)	(fluoride) 1 mg/l	2.2 mg/l
Sodium phosphate ($NaH_2PO_4.H_2O$)	(Phosphate) 0.04 mg/l	0.18 mg/l
Calcium chloride ($CaCl_2$)	(calcium) 40 mg/l	111 mg/l
Sodium bicarbonate($NaHCO_3$)	–	250 mg/l
Sodium arsenite ($NaAsO_2$.)	As(III) = 0.050 mg/l	0.087 mg/l
Temperature	20 °C ± 2.5 °C	–
Turbidity	< 1 Nephelometric turbidity unit (NTU)	–
pH	6.5 ± 0.25 and 8.5 ± 0.25	–
Dissolved Oxygen	<0.5 mg/l	–

input and output parameters have many similarities. Tables 10.1 and 10.2 below show the composition of input challenge test water used for arsenic (III and V) removal from the iron oxide granule filter.

As per protocol, to qualify for an arsenic reduction claim, a water treatment system shall pass the test for pentavalent arsenic reduction and shall pass a separate test for trivalent arsenic reduction at two different pH conditions (6.5 and 8.5). Claims may be made for pentavalent only and for arsenic reduction (As-III as well as As-V). A claim for only trivalent arsenic reduction shall not be made.

10.2.4 Toxicity Characteristic Leaching Procedure (TCLP)

This test is performed as per TCLP protocol US-EPA method 1311 to check the acid neutralization capacity of the experimental waste (arsenic loaded iron oxide media from the spent filter). Those with low acid neutralization capacity are extracted with TCLP solution no.1 (i.e. 0.1 M sodium acetate buffer, pH 4.93 ± 0.05) and those with high acid neutralization capacity are extracted with TCLP solution no.2 (i.e. 0.1 M acetic acid, pH 2.88 ± 0.05).

100 g of the dry media (arsenic-iron oxide-waste from the spent filter) was taken by sieving through a 9.5 mm sieve and transfer to an extraction bottle. Add 2 l of TCLP solution (No. 1 or 2 as determined by preliminary evaluation) and close the extraction bottle. Rotate the extraction bottle in an agitating apparatus at 30 rpm for 20 h at a temperature of 23 ± 2 °C. After completion of the agitation, filter it through a glass fibre filter (0.6–0.8 micrometre pore size). Collect the filtrate and record its pH. Take 3 aliquot samples from the filtrate for the determination of arsenic concentration. Immediately acidify each aliquot samples with nitric acid to a pH little less

Table 10.2 Composition of input challenge test water for 150 ppb arsenic (V)

Source	Parameter	Addition of salt (mg/l)
Sodium silicate ($Na_2SiO_3.9H_2O$)	(Silica) 20 mg/l	93 mg/l
Sodium nitrate (NaNO3)	(Nitrate) 2.0 mg/l	12 mg/l
Magnesium sulphate ($MgSO_4.7H_2O$)	(Magnesium) 12 mg/l	128 mg/l
Sodium fluoride (NaF)	(Fluoride) 1 mg/l	2.2 mg/l
Sodium phosphate ($NaH_2PO_4.H_2O$)	(Phosphate) 0.04 mg/l	0.18 mg/l
Calcium chloride ($CaCl_2$)	(Calcium) 40 mg/l	111 mg/l
Sodium hypochlorite (NaCIO)	(Free available chlorine) 0.5 mg/l	0.125 ml/l
Sodium bicarbonate($NaHCO_3$)	–	250 mg/l
Sodium arsenate ($NaHAsO_4.7H_2O$)	0.150 mg/l	0.54
Temperature	20 °C ± 2.5 °C	–
Turbidity	<1 Nephelometric turbidity unit (NTU)	–
pH	6.5 ± 0.25 and 8.5 ± 0.25	–

than 2. Analysis of arsenic in aliquot and filtrate is done by inductively coupled plasma (ICP-MS) spectroscopy measurements.

Arsenic concentration in the extracting solution during testing must be less than 5 mg/l in order to be considered a non-hazardous waste and safe for municipal solid waste landfill disposal.

10.3 Results and Discussion

The source of iron oxide fine powders used here for the purpose of arsenic removal is generated as a waste from steel manufacturing plant which also poses disposal problem in an eco-friendly manner. However, the use of fine powder of iron oxide for water filtration application could pose following difficulties such as, (a) flow water through a device that is densely packed with fine powders, (b) combining other porous medium like sand or carbon in conjunction with iron oxide powder will lead to less amount of active medium (iron oxide fines) thus, limiting the arsenic adsorption capacity for long term performance. Iron oxide powder used for the current application is characterized as shown in Table 10.3.

It is found that in the iron oxide obtained from the steel plant waste composed of 90–95% of iron oxide with a BET surface area of more than 50 m2/g and the particles are found to be ranging from nano size to submicron size (Table 10.3). Characterization of iron oxide particle using XRD reveals the x-ray peaks matching with standard diffraction pattern for alpha-Fe_2O_3 (Fig. 10.2).

Dynamic light scattering method was employed to measure the particle size distribution of iron oxide powder (Fig. 10.3a). The particle size analysis done in a

Table 10.3 Basic characterization of iron oxide powder

% Iron oxide (XRF)	Surface area (BET)	Tap density	Particle Size Distribution (DLS)
90–95% Iron oxide	56 m2/g	0.9 cc/g	200 to >1000 nm

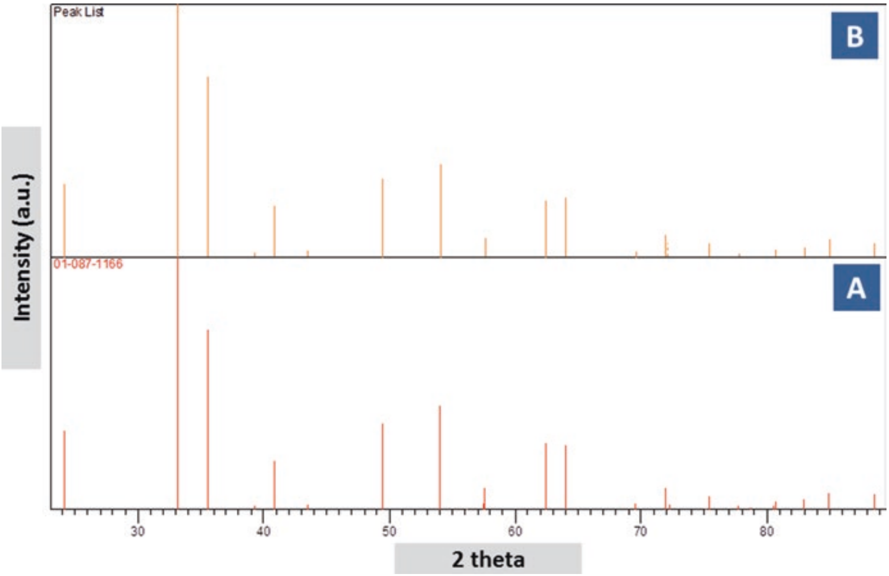

Fig. 10.2 X-ray diffraction measurement. (**a**) Standard diffraction pattern for alpha-Fe2O3 and (**b**) diffraction pattern of iron oxide powder obtained from a steel manufacturing waste

Malvern DLS instrument by dispersing 0.5% of iron oxide powder in distilled water and ultrasonicated for 5 min. Particle size distribution of iron oxide is found to be in the range of 200 nm to >1000 nm. Additionally, zeta potential measurement of iron oxide powder was done (Fig. 10.3b) in order to study the surface charge present on the particle. Zeta potential of 48.7 mV (±7.7) indicates high positive charge on the particle surface.

10.3.1 Details of Iron Oxide Granule Formation and Characterization

The use of fine powder of iron oxide can restrict arsenic removal application due to the fact that it is difficult to flow arsenic rich water through a device that is densely packed with fine powders. Therefore, to address this issue, a novel methodology was developed to synthesize granules of iron oxide fine powders using a biopolymer

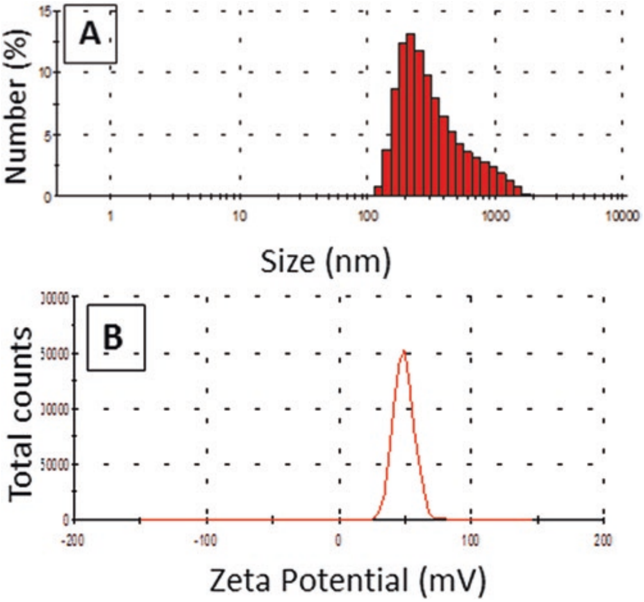

Fig. 10.3 (**a**) Particle size distribution of iron oxide particles; (**b**) Zeta potential measurement of iron oxide particles

–chitosan. The method of granule preparation is explained in the experimental section which follows various steps of first mixing iron oxide powders in chitosan solution dissolved in acidic pH water followed by polymerization of chitosan by increasing pH of the solution. This helps in binding individual particles of iron oxide in the presence of chitosan polymeric matrix (Gang et al. 2010; Jiang et al. 2013; Liu et al. 2010). With this, the individual iron oxide fine particles are glued together to form desired sized granules (Fig. 10.4).

These iron oxide-chitosan granules formed are porous and when come in contact with water, they swell indicating water entering the granules easily. The easy access of water to the granules will be helpful in arsenic ions in the water to come in contact with iron oxide particles for better adsorption. Analysis revealed that the iron oxide particle morphology and size remained intact even after granulation.

Scanning electron micrograph studies of iron oxide nanoparticles and granules (made out of this powder) was carried out and shown in Fig. 10.5. This characterization is essential in order to understand if there is any effect/change in particle size/morphology of the iron oxide powder during granule making process that may restrict/reduce granules performance vs. virgin iron oxide.

SEM micrograph of iron oxide fine powder at different magnification is shown in Fig. 10.5a, b. The SEM images indicate individual iron oxide nanoparticles distributed in a closed packed aggregate. SEM micrograph of iron oxide-chitosan granules at different magnification is shown in Fig. 10.5c, d. It is found from the SEM analysis that the particle morphology and size seems to be intact even after granulation.

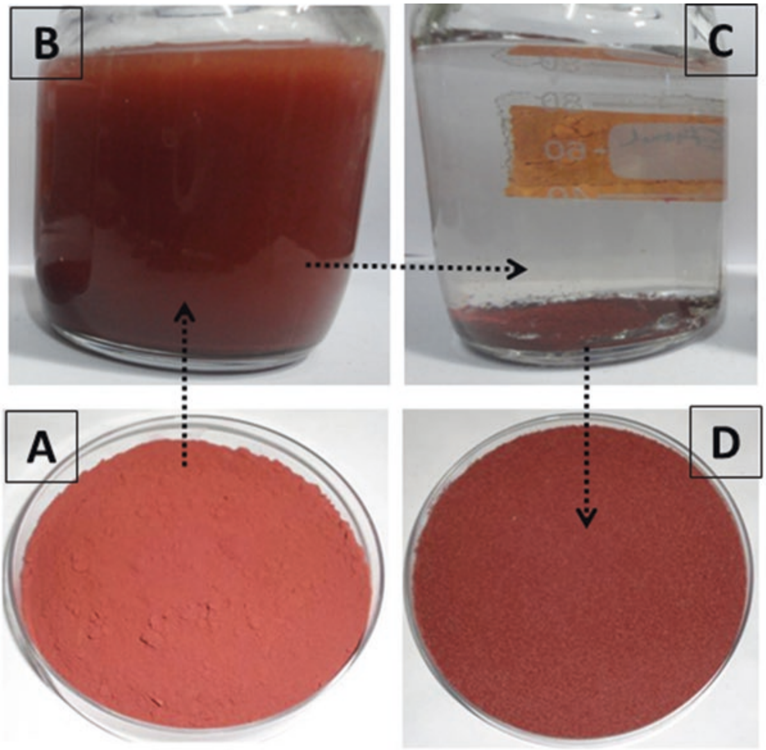

Fig. 10.4 (**a**) Photograph of iron oxide powder; (**b**) Photograph of Iron oxide-chitosan complex dispersed in water; (**c**) Iron oxide-chitosan complex controlled precipitation from reaction mixture to form granules; and (**d**) Photograph of dried iron oxide granules

Figure 10.6 illustrates thermo gravimetric analysis of the iron oxide particles and iron oxide-chitosan granules. Thermo gravimetric analysis of iron oxide particles indicates minimal weight loss. Whereas, thermo gravimetric analysis of the granules indicates weight loss of approximately 15%, this is attributed to the fact that the granules are composed of 85% (w/w) of iron oxide particles and 15% (w/w) of the chitosan.

The iron oxide granules are advantageous as large amount of iron oxide can be packed in a filtration column/ block thus avoids combining the use of other media such as carbon, and sand. Dried iron oxide granules is seen to swells when come in contact with water and gives a spongy feel, implies accessibility of water into the granules. The swelling property of granules is advantageous to pack them in a loose bed with appropriate mesh support. The biopolymer (chitosan) used for the granulation was carefully selected, also adsorbs arsenic thus playing synergistic effect with iron oxide for the arsenic removal (Gang et al. 2010; Jiang et al. 2013; Liu et al. 2010). Post granulation and separation of desired fractions (150 microns to 1 mm), these iron oxide granules are housed in a column (500 mm height × 50 mm diameter) with a specially designed mesh cap (5 microns pore) and is evaluated for arsenic removal efficacy using NSF-53 and US-EPA guidelines.

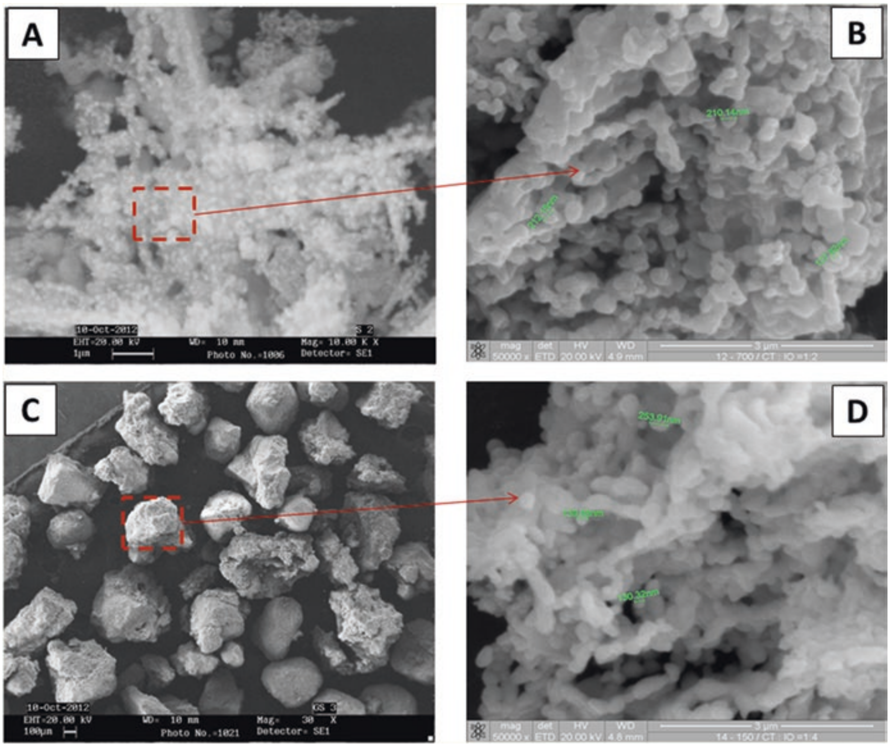

Fig. 10.5 (**a**, **b**) SEM micrographs of iron oxide fine powder at lower and higher magnifications; (**c**, **d**) SEM micrographs of iron oxide granules at lower and higher magnifications

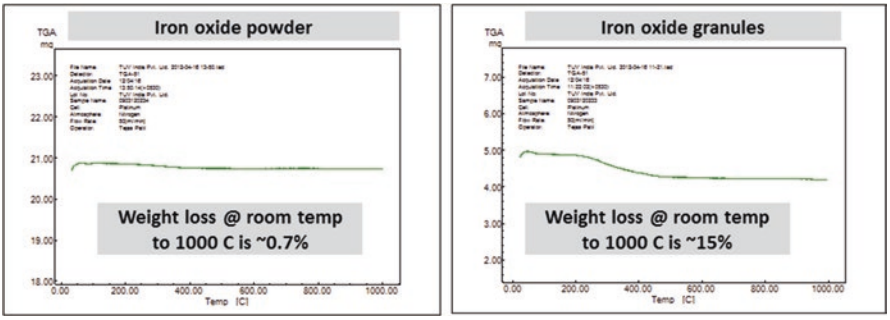

Fig. 10.6 Thermo gravimetric analysis of iron oxide powder and granules

Table 10.4 Iron leaching analysis from 2 numbers of random filters tested over filtration volume of 1000 l of water

Fe leaching- ICP MS measurements (Filter 1)		Fe leaching- ICP MS measurements (Filter 2)			
Sr. No.	Water passed in Liter	Fe in ppb	Sr. No.	Water passed in Liter	Fe in ppb
1	10	<10	1	20	<10
2	90	<10	2	110	13
3	180	<10	3	190	<10
4	310	<10	4	240	<10
5	420	<10	5	350	<10
6	560	<10	6	420	15
7	690	11	7	590	<10
8	810	12	8	710	15
9	920	14	9	890	12
10	1005	15	10	1012	14

10.3.2 Iron Leaching Test

In order to understand the leaching of iron oxide particles from the filtration column, tests were conducted by collecting output water from 2 random filters at different volume of water flow over a life of 1000 l. As per standard guidelines, minimum iron leaching in the output water allowed is ~1000 ppb (1 ppm). Table 10.4 below illustrates iron leaching analysis from 2 numbers of random filters tested over filtration of 1000 l. Inductively coupled plasma spectroscopy was employed to measure iron content in the output water. It is clear from the Table 10.4 that iron leaching is well below than the stipulated allowance limit.

10.3.3 Adsorption Efficiency of Iron Oxide Granules

For arsenic removal efficiency of the filtration device, USEPA advocates use of any input arsenic concentration of your choice based on local ground water contaminations level and reduce it to less than 10 ppb and claim the same conditions in the product (e.g. this product meets US EPA standard for arsenic with an input of say 200 ppb arsenic). Waters containing naturally occurring arsenic are preferable over synthetic water spiked with arsenic. US-EPA also suggests on using local ground water (arsenic contaminated) as the input source, however in case it is not available, one can choose appropriate input arsenic concentration and follow the standard protocol.

In this study, 12 numbers of columns containing iron oxide granules were fabricated and installed in the arsenic testing platform to evaluate arsenic removal ability of these filters as per NSF-53/US EPA testing guidelines (as explained in the experimental section). Each cylindrical column is packed with 200 g of iron oxide granules containing granule size ranging 150 microns to 1 mm size. As per standard protocol, to qualify for an arsenic reduction claim, a water treatment system shall pass the test for pentavalent arsenic reduction and shall pass a separate test for trivalent arsenic reduction at two different pH conditions (i.e. 6.5 and 8.5). Claims may be made for pentavalent only or for total As reduction (As-III as well as As-V). A claim for only trivalent arsenic reduction shall not be made, suggests the guidelines.

For trivalent arsenic (As-III) reduction test, input challenge test water including 50 ppb of sodium arsenite was made as per composition given in Table 10.1 (experimental section). As per the test protocol, the above input water composition would be prepared at two different pH (6.5 and 8.5) conditions. Table 10.5 below shows the evaluation of 3 numbers columns containing 200 g each iron oxide granules passed through its life of ~1000 l of input challenge water comprising 50 ppb of sodium arsenite (As -III). The pH of the above water composition was maintained at pH 6.5.

Table 10.6 below shows the evaluation of 3 numbers columns containing 200 g each iron oxide granules passed through its life of ~1000 l of input challenge water comprising 50 ppb of sodium arsenite (As -III). The pH of the above water composition was maintained at pH 8.5.

For pentavalent arsenic (As-V) reduction test, input challenge test water including 150 ppb of sodium arsenate was made as per composition given in Table 10.2

Table 10.5 The performance evaluation of 3 numbers of iron oxide granule columns passed through its life of ~1000 l of input challenge water comprising 50 ppb of sodium arsenite, As (III) at pH 6.5

Filter no.	10 bed volume water passed in Liter.	As in ppb (Output water)	Water passed in Liter. (~25% Life)	As in ppb (Output water)	Water passed in Liter. (~50% Life)	As in ppb (Output water)	Water passed in Liter. (~75% Life)	As in ppb (Output water)	Water passed in Liter. (~100% Life)	As in ppb (Output water)
1	31	0	260	0–5	556	0–5	776	5–10	1030	5–10
2	35	0	252	0–5	527	5–10	735	5–10	1089	5–10
3	34	0	265	0	553	0–5	806	0–5	1062	5–10

Table 10.6 The performance evaluation of 3 numbers of iron oxide granule columns passed through its life of ~1000 l of input challenge water comprising 50 ppb of sodium arsenite, (As-III) at pH 8.5

Filter no.	10 bed volume water passed in Liter.	As in ppb (Output water)	Water passed in Liter. (~25% Life)	As in ppb (Output water)	Water passed in Liter. (~50% Life)	As in ppb (Output water)	Water passed in Liter. (~75% Life)	As in ppb (Output water)	Water passed in Liter. (~100% Life)	As in ppb (Output water)
4	38	0	257	0	492	5–10	724	5–10	1002	5–10
5	36	0	254	5–10	552	5–10	769	5–10	1032	5–10
6	30	0	251	0	559	5–10	756	0–5	1018	5–10

Table 10.7 The performance evaluation of 3 numbers of iron oxide granule columns passed through its life of ~1000 l of input challenge water comprising 150 ppb of sodium arsenate, As (V) at pH 6.5

Filter no.	10 bed volume water passed in Liter.	As in ppb (Output water)	Water passed in Liter. (~25% Life)	As in ppb (Output water)	Water passed in Liter. (~50% Life)	As in ppb (Output water)	Water passed in Liter. (~75% Life)	As in ppb (Output water)	Water passed in Liter. (~100% Life)	As in ppb (Output water)
7	33	0	230	0	527	5–10	748	0–5	1034	10–25
8	32	0	286	0–5	558	5–10	731	10–25	1009	10–25
9	39	0	272	0–5	545	10–15	786	5–10	1021	10–25

Table 10.8 The performance evaluation of 3 numbers of iron oxide granule columns passed through its life of ~1000 l of input challenge water comprising 150 ppb of sodium arsenate, As (V) at pH 8.5

Filter no.	10 bed volume water passed in Liter.	As in ppb (Output water)	Water passed in Liter. (~25% Life)	As in ppb (Output water)	Water passed in Liter. (~50% Life)	As in ppb (Output water)	Water passed in Liter. (~75% Life)	As in ppb (Output water)	Water passed in Liter. (~100% Life)	As in ppb (Output water)
10	36	0	251	5–10	494	5–10	767	5–10	1005	5–10
11	34	0	239	5–10	498	5–10	725	10–25	1049	10–25
12	29	0	244	5–10	516	5–10	751	5–10	1082	10–25

(experimental section). As per the test protocol, the above input water composition would be prepared at two different pH (6.5 and 8.5) conditions. Table 10.7 below shows the evaluation of 3 numbers columns containing 200 g each iron oxide granules passed through its life of ~1000 l of input challenge water comprising 150 ppb of sodium arsenate (As-V). The pH of the above water composition was maintained at pH 6.5.

Table 10.8 below shows the evaluation of 3 numbers columns containing 200 g each iron oxide granules passed through its life of ~1000 l of input challenge water comprising 150 ppb of sodium arsenate, As(V). The pH of the above water composition was maintained at pH 8.5.

Each data point presented in the performance evaluation chart (Tables 10.5, 10.6, 10.7, 10.8) is the average of 3 separate measurements done for arsenic quantification. As per the standard protocol, output water from the arsenic filtration device to be evaluated in 5 intervals of the filters total life. That means the arsenic removal efficacy to be tested after the filtration device passed through minimum 10 bed volumes of water and at its life of 25%, 50%, 75% and 100%. Performance evaluation (Tables 10.5, 10.6, 10.7, 10.8) of As (III) and As (V) at pH 6.5 and 8.5 over a volume of 1000 l filter life, we have demonstrated the ability of iron oxide-chitosan granules in successfully reducing arsenic from water and help making water potable.

The biopolymer (chitosan) not only helped in the iron oxide granulation but also helped in removal of arsenic from water. Chitosan presence was advantageous in many ways such as it acts as a binder for the granule formation, its water absorption capability helped making the granules soft thus avoid granule disintegration, it allowed water molecules to permeate through the granules thus allowing arsenic ions to come in contact with iron oxide particles and finally, it is also believed to have played a synergistic role of binding arsenic ions along with iron oxide nanoparticles. The affinity of iron oxide granules media for arsenic ions was shown to be strong under both the pH (6.5 and 8.5) conditions. This feature allows iron based sorbents to treat more bed volumes and considered to be the best media to filter arsenic from arsenic rich water (Gang et al. 2010; Jiang et al. 2013; Liu et al. 2010).

10.3.4 Safe Disposal of Spent Arsenic Media using TCLP

TCLP determines hazardous or non-hazardous nature of the spent arsenic filter media. As per US EPA TCLP guidelines, arsenic concentration in the extracting solution from the spent filter during testing must be less than 5 mg/L in order to be considered a non-hazardous waste and safe for municipal solid waste landfill disposal.

Leaching study of iron oxide granules recovered from arsenic filter columns after passing through ~1000 l of spiked arsenic water was done following USEPA TCLP method-1311. Random filters were selected for the TCLP studies. Spent iron oxide granules containing arsenic after 1000 l of water passed are analysed by ICP-MS to estimate the concentrations of arsenic present in TCLP extracts as per protocol explained by USEPA.

All the leaching studies conducted from the spent iron oxide granules containing arsenic were found to be well below the specified limit (Table 10.9). Therefore, we have successfully tested the mechanism for the safe disposal of exhausted /spent filters, which has passed the TCLP as per US EPA guidelines enabling it to be disposed of in a municipal solid waste landfill.

Table 10.9 TCLP studies of spent arsenic filtration media

Filter numbers	Quantification of Arsenic loaded in granules (ppm)	Quantification of Arsenic remained in granules after TCLP treatment (ppm)	Arsenic leached from the spent filter (TCLP extract) (ppb)
1	93.92	76.38	17.04
2	50.64	42.23	13.9
4	101.03	99.41	36.05
5	97.14	99.96	25.1
7	219.25	199.7	78.85
8	206.06	203.05	79.5
10	135.04	128.34	40.1
11	132.35	133.29	44.55

10.4 Conclusions

We have shown the development of a novel methodology to synthesize granules of iron oxide nanoparticles using a biopolymer. These granules are porous leads to easy access of water to the granules allowing effective binding of arsenic present in the water. The basic advantages with the granulation of iron oxide is that it allows large amount of active ingredient (~85% –iron oxide) that can be packed in a cartridge/ block thus avoid combining the use of any other media such as carbon and sand. The biopolymer used as an aid for the granulation also helps in adsorbing arsenic thus playing synergistic effect with iron oxide for the arsenic removal from drinking water. Post granulation and separation of desired iron oxide granule fractions, these granules are housed in a column with a specially designed mesh support and evaluated for arsenic removal efficacy using NSF-53 and US-EPA guidelines. 12 columns with granules have been tested with an input of 200 ppb arsenic (150 ppb As– V and 50 ppb As –III) at two different pH conditions (6.5 and 8.5). Over a volume of 1000 l of water passed through these columns containing iron oxide granules, a basic understanding of the performance of iron oxide granules in reducing arsenic was established. We believe that significant improvements in the output performance can further be achieved by emphasizing the process engineering and designing aspects of the device.

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