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Green synthesis of α-Fe_2O_3 nanoparticles for arsenic(V) remediation with a novel aspect for sludge management

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ABSTRACT

A simple, single step and eco-friendly approach was taken for synthesizing iron oxide nanoparticles using *Aloe vera* leaf extract. The nanoparticles were characterized by various techniques and used for arsenic(V) remediation in synthetic system with an initial concentration range of 2–30 mg/L. The effect of pH, particle dosage and initial arsenic concentration on arsenic adsorption was investigated using response surface methodology involving five levels Central Composite Design (CCD) considering adsorption capacity as the response. The nanoparticles showed a high sorption capacity of 38.48 mg/g in the experimental range of concentration compared to other inorganic oxide based adsorbents.

A novel approach was adopted for utilization of arsenic contained sludge. As(V) sorbed nanoparticles were used in the preparation of colored soda lime silicate glass. The basic properties such as density, thermal and optical properties were measured for the experimental glass sample and compared with samples containing commercial Fe_2O_3.

The overall study indicates that the green synthesized iron oxide nanoparticle is a prospective candidate for arsenic remediation in contaminated water. The arsenic contained sludge may be used in preparation of coloured glasses which have wide application in making container bottles and building glasses.

1. Introduction

Nanotechnology has introduced a new dimension in the field of environmental remediation of various toxic contaminants like heavy metals, dyes and pesticides etc. Controlling the particle size and shape at nanoscale results into a large surface area to volume ratio which imparts greater reactivity. Apart from the smaller particle sizes, presence of a large numbers of active sites and the catalytic potential of nanoparticles enable them as potential candidates for wide range of contaminants [1]. Nanoscale iron particles have shown efficiency for detoxification of chlorinated organic solvents, organochlorine pesticides and PCBs [2]. Zhang et al. prepared ferromagnetic carbon coated Fe nanoparticle which could remove over 95% of chromium (VI) in wastewater [3]. Manganese based nanoparticle synthesized using micro-emulsion process and coated with gold was observed as efficient nano-sorbents for removal of heavy metals from wastewater [4]. Copper (II) oxide nanoparticles synthesized by thermal refluxing process were found as a potential nano-adsorbent for arsenic removal [5].

Iron oxide based components have a natural affinity for arsenic sorption [6]. Removal of As(V) using magnetic Fe_3O_4 from municipal waste water has been reported [7]. Fe(III) crosslinked alginate nanoparticles were used in fixed bed column for arsenic (V) removal [8]. Apart from being an effective adsorbent of As(V), the nano-sorbent demonstrated antimicrobial property also. The adsorption–desorption behaviour for As(V) was studied using hydrated iron oxide particles in combination with a macroporous ion-exchange resin at neutral pH [9]. A novel composite material was developed with high arsenic adsorption capacity by encapsulating γ-Fe_2O_3 nanoparticles in macroporous silica [10].

Most of the research studies focus on synthesis of iron oxide nanoparticles by chemical route using reducing agents [11]. Chemical reagents are often toxic, flammable and expensive in nature. In the process of synthesizing magnetite nanoparticles using toxic solvents, hazardous byproducts may generate and the process involves high energy consumption [12]. Therefore, biogenic or green synthesis of nanoparticles has emerged as an environment friendly and promising approach. Application of

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various plant extracts has been reported for biosynthesis of gold and silver nanoparticles using rapid and nontoxic process [13]. Presence of different phytochemicals, viz. glutathiones, polyphenols, alkaloids as well as various types of proteins, enzymes, polysaccharides and alcoholic compounds in plant extracts facilitate reduction of metal ions and formation of stable nanoparticles [12]. Extracts of *Aloe vera* leaves were used for production of silver nanoparticles and its antimicrobial activity has been studied [14]. The gel of *A. vera* leaf acts as a bio-reducing agent for preparation of metal oxide and metal nanoparticle, semiconductors, etc. [15]. Nanocrystalline zinc-aluminate had been synthesized using *A. vera* leaf extract [15]. Biosynthesis of iron oxide nanoparticles with less than 5 nm were achieved in preferential cubic arrays deriving into magnetite and wuestite-like clusters using alfalfa [16].

The present study is oriented towards developing an effective and eco-friendly solution using iron oxide nanoparticles for arsenic remediation in highly arsenic contaminated water. Although various morphologies of haematite crystals had been developed earlier [17–19], however the necessity for developing a simple and appropriate method for synthesis of controlled sized hematite crystals still exists [11]. In the current study haematite (α-Fe_2O_3) nanoparticles have been synthesized using a simple and single step green procedure using *A. vera* plant extract. Leaf extracts of *A. vera*, a traditional medicinal plant containing various phytochemicals like flavonoids, tannin, saponin, sterols along with organic acids, polysaccharides and different enzymes [20]. Although the plant extract had been used in synthesis of gold and silver nanoparticles [21,22], phytogenic synthesis of α-Fe_2O_3 nanoparticles using *A. vera* extract has not been reported till date. In the present study green synthesis of α-Fe_2O_3 nanoparticles (FeIII-NP) has been attempted using *A. vera* leaf extract and the potential of the synthesised nanoparticles has been explored for arsenic(V) remediation in synthetic aqueous system. This method of synthesis employs cost-effective, environment friendly, non-toxic precursors and is a simple and time saving process [15] unlike the conventional chemical routes. Response surface methodology (RSM) was employed using the As(V) adsorption capacity of developed nanoparticles as the response to optimize different parameters involved in arsenic adsorption, viz. solution pH, nanoparticle dosage and initial arsenic concentration. The statistical analysis based on Central Composite Design (CCD) was undertaken to evaluate the overall interactive influences on the experimental response and to identify the relationship between the response and the independent variables in an efficient manner compared to the conventional processes.

Sludge management in arsenic remediation technologies is a major issue which needs special attention from the environmental perspectives. As the arsenic rich sludge cannot be disposed to landfill, the objective is to reuse the sludge for beneficial purpose. Application of ingredients like lime, cement, clay, etc. had been reported for solidification of the sludge in producing construction materials like bricks [23]. A novel application had been explored for arsenic sludge management in the present study. As(V) containing α-Fe_2O_3 nanoparticle sludge was utilized in the preparation of coloured soda lime silicate glass. Generally iron is avoided in common glass making. However for special/functional glasses like amber glasses, heat absorbing glasses and container glasses, iron needs to be incorporated. This motivated us to use the arsenic contaminated iron oxide sludge in glass making. Presence of As(V) acts as a refining agent [24] and helps in the reduction of bubbles during melting, thus facilitates homogenization of the glass sample. The basic properties such as density, thermal and optical properties of the glass sample were measured along with examination of bubbliness and compared with that of soda lime silicate glass prepared with doping of commercial Fe_2O_3. The produced glass may have a wide application in container bottles and also as building glasses.

2. Materials and methods

2.1. Synthesis of nanoparticles

Anhydrous ferric chloride ($FeCl_3$) of AR grade obtained from Merck, Germany was used as the initial precursor. *A. vera* leaves were collected from nearby garden and washed thoroughly with distilled water to eliminate dust and other surface impurities. The leaves were cut into small pieces, ground and boiled with small amount of distilled water for 10 min to obtain a thick, viscous gel which was subsequently filtered and stored at cold condition. 10 g anhydrous $FeCl_3$ was added to 100 cc of this extract with 1:10 w/v ratio and kept under heating and stirring mode at 250 °C and 300 rpm respectively. Heating was conducted in a closed conical flask. Change of colour from yellow to brownish black was observed within about 10 min indicating formation of iron oxide nanoparticles. The solution was evaporated to dryness to separate the formed nanoparticles. The particles were washed with distilled water for several times and centrifuged to separate the supernatant. The material obtained was dried in air oven and kept in air tight container for further use.

2.2. Characterization of nanoparticles

The synthesised nanoparticles were characterized by X-ray Diffraction technique to predict the crystallinity as well as the phase of the compound. The XRD analysis was performed using Philips 1710 diffractometer with starting position $2\theta = 20.02°$ to end position $2\theta = 79.97°$ having step size $2\theta = 0.05°$ using Cu as anode material ($\alpha = 1.541$A°) at 25 °C. The morphology and microstructure of the powder material was studied using field emission scanning electron microscopy (FESEM, Zeiss, Germany). In addition, the qualitative energy dispersive spectroscopy (EDS) spectra analysis was undertaken to know the elemental composition of the particles. The morphology of the powder was further confirmed by Transmission Electron Microscopy (TEM) analysis (Technai G2, 30ST (FEI, USA) instrument). The oxidation states of iron and oxygen in the synthesized nanoparticle was analyzed by X-ray photoelectron spectroscopy technique using PHI 5000 XPS-analyzer, (Versaprobe-II, USA). The particle size of the synthesized powder was measured using particle size analyzer (Zetasizer, Nanoseries, Malvern). Specific surface area of nanoparticle was determined by adsorption–desorption of nitrogen using multi-point Braunauer–Emmett–Teller (BET) method using Quantachrome Autosorb Automated Gas Sorption System, (USA). Fourier transform infrared spectroscopy (FTIR, PerkinElmer, USA) was employed for identification of various functional groups in the synthesized FeIII-NP within the range of 400 cm^{-1}–4500 cm^{-1}. The arsenic adsorbed nanoparticle sample was characterized in terms of FTIR and FESEM analysis to identify any possible changes in FeIII-NP after arsenic sorption.

2.3. Batch mode study with arsenic(V) and optimization of process parameters by response surface methodology

Standard As(V) solution of 1000 mg/L obtained from Merck, Germany was used as the stock solution for adsorption experiments. As(V) solution of a certain initial concentration was taken in 50 mL conical flasks, pH was adjusted and FeIII-NP was incorporated at a certain dosage. The solutions were stirred at 150 rpm for 12 h in controlled temperature, filtered using 0.2 μm PVDF disposable syringe filters and analysed for As(V) concentration