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Synthesis of Magnetite Nanoparticles for Arsenic Removal from Ground Water Pond

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Abstract: Magnetite nanoparticles were synthesized by chemical co-precipitation technique from $FeCl_2$. The structure, morphology and magnetic properties of magnetite were characterized by X-ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Vibrating Sample Magnetometer (VSM). The result of XRD spectral pattern with characterization was indicated the presence of Magnetite nanoparticles. SEM micrograph of the Magnetite nanoparticles showed in the nano range of size has average diameter 26.78 nm. Magnetic characteristic of Magnetite nanoparticles was indicated super paramagnetic properties. The saturation magnetic was 90.01 emu g^{-1}. Therefore, the Magnetite nanoparticles are suitable to remove arsenic in the water by a simple magnetic adsorption process. It was found that as the removal efficiency of Arsenic from ground water by magnetite nanoparticles in highest adsorption of 95% was achieved.

Keywords: Magnetite nanoparticles, SEM analysis, FTIR spectral analysis, XRD analysis, Arsenic.

Introduction

Arsenic (As) is the twentieth most abundant element in the earth’s crust, fourteenth in seawater and it is the twelfth most abundant element in the human body[1]. Arsenic is a contaminant of well-known toxicity and it is not an uncommon contaminant in ground waters, air and living beings (sea-living species) [2]. Although arsenic is necessary as a nutrient to humans in small quantities, it also leads to death in chronic intakes[3].

Most of the arsenic present in the nature is in the As (V) form that has relatively low toxicity. However in contact with the air it generates oxidized forms which are more toxic. The health effects have a large diversity, from skin pigmentation, skin damages to skin and respiratory cancer. Arsenic may be found in water that has flowed through arsenic wealthy rocks. Brutal health effects have been found in populations drinking arsenic-rich water over long periods in countries world-wide[4].

The most important source of arsenic exposure is ingestion of drinking water, and the arsenic levels are generally highest in groundwater, especially where geochemical conditions favor the dissolution of arsenic[5]. In six districts of West Bengal, India, the arsenic levels in groundwater, where the source of arsenic is geological, have been found above the maximum allowable limit (50 $\mu g l^{-1}$).

Arsenic in water supplies causes chronic poisoning rather than acute poisoning; therefore, chronic toxicity of arsenic is of main concern in the evaluation of health significance of arsenic in drinking water[6]. Chronic arsenic poisoning leads to non-specific symptoms including chronic weakness, loss of reflexes, gastritis, anorexia, weight loss, hair loss, and long term exposure results in hyper pigmentation, disturbance in nervous systems, cardiovascular diseases and circulatory disorders. The frequent symptoms of acute arsenic poisoning are vomiting, dryness of the mouth and throat, muscle cramps, circulatory disorders, nervous weakness, hallucinations, and fatal shock can develop due to renal failure[7]

Several methods are used to remedy arsenic contamination. Those treatment methods are adsorption, electrochemical reduction, ion exchange, nano-filtration, precipitation, solvent extraction and reverse osmosis[8]. However, as recently noted, these technologies do not perform well in actual field trials and improved systems are needed[9]. As (III) adsorption on different sorbents such as coconut husk carbon, carbon from fly-ash, iron-oxide-coated polymeric material, and hybrid polymeric sorbent has been examined [10, 11].

Iron and iron-coated sand, iron-coated activated carbon[12] and granular ferric hydroxides[13] have also been used as adsorbents. However, their use is limited due to sludge formation, high operation cost and technical difficulties in the preparation of materials. Naturally occurring ores and minerals, namely kaolinite[14], magnetite[15, 16], maghemite[17], hematite, and feldspar[18], have also been used for the adsorption of arsenic though not as extensively as other materials. Magnetite–maghemite (Fe_3O_4–c-Fe_2O) nanoparticles are potential sorbents for arsenic removal in drinking water and are therefore suitable for treating arsenic-contaminated water.

Many authors prepared Magnetite at its different properties, but still Magnetite inspire researcher's new researchable ideas, due to its characteristics that has a great significance in various fields, especially in a nano-size[19].

Magnetite (Fe) nanoparticles have attracted much interest not only in the field of magnetic recording media such as audio and videotape, magnetic fluids, high density digital recording disks, data storage[20], but also in the areas of medical care such as drug delivery systems (DDS), medical applications including radio frequency hyperthermia, magnetic resonance imaging (MRI) and photomagnetics, medical diagnostics and cancer therapy and high frequency applications, microwave devices, sensors, magneto-optics devices, catalysis and magnetic sensing[21]. The objective of the present study was to synthesis the magnetite nanoparticles from chemical method and it used for evaluating the efficacy of Arsenic removal from ground water.

Materials and Methods

Stock Preparation

0.5M Molar Ferric chloride: 608.175 mg of $FeCl_3 \cdot 6H_2O$ dissolved in 4.5 ml of distilled water. 2 M HCl solution: 50 µ l of concentrated HCl dissolved in 0.05 ml of double distilled water. 0.3 M Na_2SO_3: 56.72 milligrams of Na_2SO_3 suspended in 1.5 ml of double distilled water

Synthesis of Magnetite nanoparticles

Prepare aqueous solution by adding 4.5 ml of 0.5 M $FeCl_3 \cdot 6H_2O$ in 0.05 ml of 2 M HCl and 1.5 ml of 0.3 M Na_2SO_3 and add to ferric chloride solution by stirring well. Meanwhile, in another clean 250 ml glass beaker, 5.08 ml of concentrated ammonia was diluted to a total volume of 80 ml with deionized water.

In the smaller beaker, the colour of solution could be seen to turn into red from light yellow immediately upon mixing Fe^{3+} and $SO3^{2-}$, implying the formation of complex ions. Then, when the colour had returned from red to yellow, the solution was quickly poured into the dilute ammonia solution under intensive stirring. After continuation of the stirring for 30 min, the beaker with the suspension was placed on a permanent magnet.

A black powder could be observed rapidly precipitating on the bottom of the beaker. The supernatant was discarded and fresh water added to the beaker. This technique was performed 5 times until a great part of the ions in the suspension had been removed. The powders were extracted by filtration and dried at room temperature.

Characterization of Magnetite nanoparticles

UV-Vis spectroscopic analysis

UV-Vis spectroscopy measurements (Shimadzu, Japan) were carried out for finding of plasmon peak for confirmation for formation of magnetite nanoparticles. The reduction of nickel ions from ferric chloride by chemical approach was monitored by measuring the absorbance of the reaction mixture in a range of wavelength from 360 to 800 nm to calculate the maximum absorbance peak of magnetite nanoparticle.

FTIR Spectrophotometer analysis

For FTIR measurements, the Magnetite nanoparticle powder synthesized from different plant mediated materials were washed three times with 20 ml of de-ionized water to get rid of the free proteins/ enzymes that are not capping the nanoparticles. The nanoparticle samples were dried in room temperature and grinded with KBr pellets and analyzed on a Shimadzu model in the diffuse reflectance mode operating at a resolution of 1 cm^{-1}.

Ferromagnetism measurement

The magnetic measurements were carried out by using magnetometer. Put the sample in the holder and connect it. Power on the deviceand slowly varies the applied magnetic field using magnetic field slider. M-H graph corresponding to the field will be plotted, whenever the slider is stopped. Calculate the loop width, the tip-to-tip height and positive intercept to negative intercept distance for each magnetic field

SEM analysis

For the SEM analysis the suspension of nanoparticles was dried into powder by critical point drier. Take about 1mg fine powder of magnetite nanoparticles were used for the morphological analysis and measure the size of the nanoparticles. SEM analysis was carried out on JEOL (SEM).

Removal of Arsenic in the drinking water by Magnetite nanoparticles

Preparation of adsorbent – Mgt nps for Arsenic removal

The magnetite nanoparticles synthesized from chemical method was used for Arsenic removal from drinking water. In a sonication bath, take the deionized water and mixed with Magnetite nanoparticles in the conc of 4g/L, the mixture was dispersed in solution for 20 min.

Collection of drinking water for Arsenic removal

Arsenic-contaminated groundwater collected from shallow pond in Perampur, Tamilandu also used in the study. After collection of water, all samples were immediately acidified with 2% HNO_3 upon collection in the field to avoid the precipitation of Fe-As compound and were kept in dark brown plastic bottles. Groundwater sample collected from shallow pond were to check the Arsenic quantity.

The Arsenic contaminated drinking water and nanoparticle mixture solution held in a slowly rotating rack of a shaker that provided a gentle end-over-end tumbling at the speed of 40 rpm for 6hrs. After shaking, the mixtures were centrifuged at 5,000 rpm for 30 min. The obtained supernatant solutions were separated and solid samples were dried in vacuum desiccators.

Then dried arsenic adsorbed magnetite nanoparticles were kept in an airtight glass container to prevent any reaction with environment. The supernatant solutions were filtered through 0.2 lm Cellulose Acetate membrane filters. The filtrate was acidified with 1% nitric acid for analysis. Atomic Absorption spectroscopy (AAS) was used to measure arsenic concentrations in the filtrate.

Results and Discussion

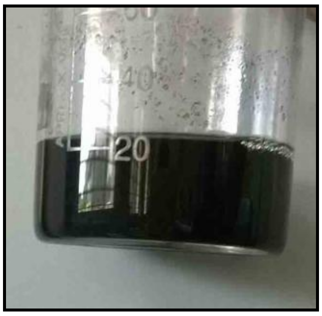

Fig. 1. Colour changes of Magnetite nanoparticles synthesized from $FeCl_2$

Colors of iron oxide are very dependent on size of nanoparticles and also indicate the chemical nature of the compound and this kind of characteristic feature is a primary attribute in their chemical identification, and also may be used checking the purity of the compound[22]. The magnetite nanoparticles synthesized from ferric chloride sample jet black in colour (Fig 1) and therefore suggesting being pure magnetite. The end of the reaction leads to form brownish-red products representing a mixture of iron oxides.

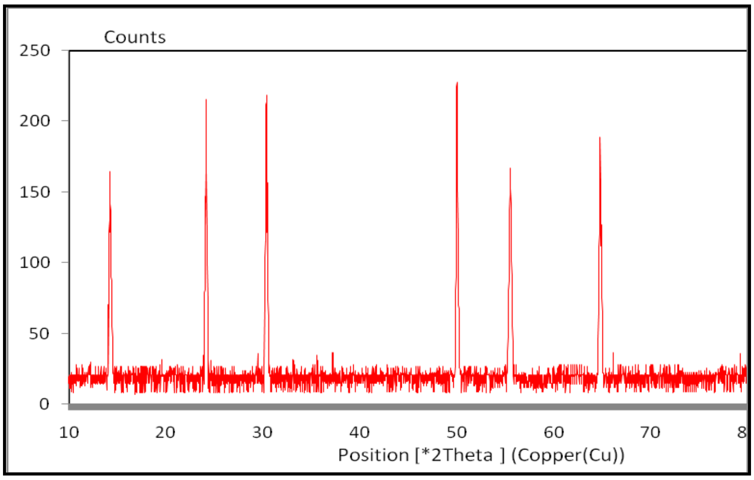

Fig. 2. XRD spectral analysis for Magnetite nanoparticles synthesized from FeCl2

Fig. 2 shows the XRD spectral patterns of the magnetite nanoparticles. Six characteristic peaks at 10.264°, 24.188°,30.364°, 49.981°, 55.483° and 64.723° were corresponding to the (165), (216), (212), (217), (149), and (135) (Table 1) crystal planes of a pure magnetite nanoparticles with a spherical structure. The XRD spectral peaks show that magnetite nanoparticles with a spherical structure and no characteristic peak of impurities are detected in the XRD spectrum[23].

Table 1. XRD Peak list for Magnetite nanoparticles synthesized from $FeCl_2$

Pos. [°2θ]	Height [cts]	FWHM Left [°2θ]	d-spacing [Å]	Rel. Int. [%]
10.264(3)	165(5)	0.18(2)	1.8760	28.23
24.188(4)	216(6)	0.22(4)	2.0134	38.56
30.364(4)	212(5)	0.22(4)	1.9843	31.78
49.981(4)	217(4)	0.23(4)	2.1954	40.31
55.483(3)	149(4)	0.16(2)	1.6756	18.32
64.723(4)	135(3)	0.15(2)	1.3464	20.54

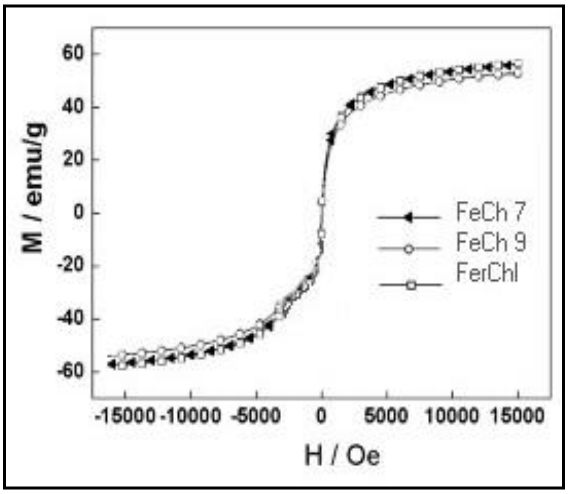

Fig. 3. Ferromagnetism measurement for Magnetite nanoparticles synthesized from $FeCl_2$

Due to small particle sizes, a XRD spectral pattern of magnetite nanoparticles is broadening presumably. From reflection curve fittings, full width at half maximum values of each reflection were used to estimate the mean coherent lengths these magnetite, using Scherrer equation, and a rough measure of the average crystallite size for all these magnetite samples is found to be about 29.33 nm.

The magnetization curve of magnetite nanoparticles obtained by magnetometer is shown in Fig. 3. The saturation magnetization of magnetitte nanoparticles was 90.01 emu g^{-1}. The magnetization of magnetite nanoparticles is 92emu g^{-1} and is not distant from its actual magnetization[24]. The outstanding magnetic property was essential for magnetic adsorption of Arsenic ontaining Ground water.

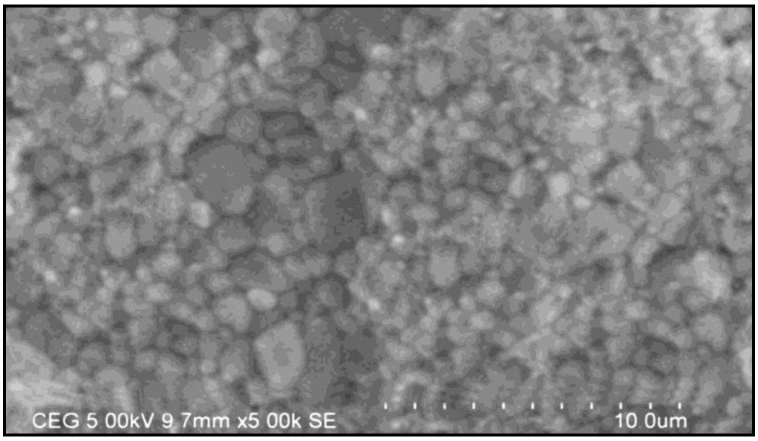

Fig. 4. SEM analysis of Magnetite nanoparticles synthesized from $FeCl_2$

The morphology and size of the magnetite particles formed is examined by direct observation through high resolution scanning electron microscopy for collected nanoparticles. The micrograph of magnetite nanoparticles is given in Figure 4. It is clearly indicated that the tested Magnetite particles are spherical, globular and sometimes in irregular in shape with a narrow size distribution and their particle sizes are in the range 16.34 nm to 54.13 nm and average particles size comes around 26.78 nm which is approximately the size calculated by the Debye–Scherrer formula.

The FTIR spectra of magnetite nanoparticles synthesized from $FeCl_2$ is shown in Fig. 5. It has been observed that the absorption band at a high wave number region (3414 cm^{-1}) is due to the OH stretching which suggests that the surfaces of the magnetite nanoparticles are covered with a number of hydroxyl (-OH) groups as is obvious and well-reported when they are prepared in the aqueous phase. As shown in the Fig. 4 at 577 cm^{-} ,' the Fe-O stretching vibration of the tetrahedral and octahedral lattice site was found[25].

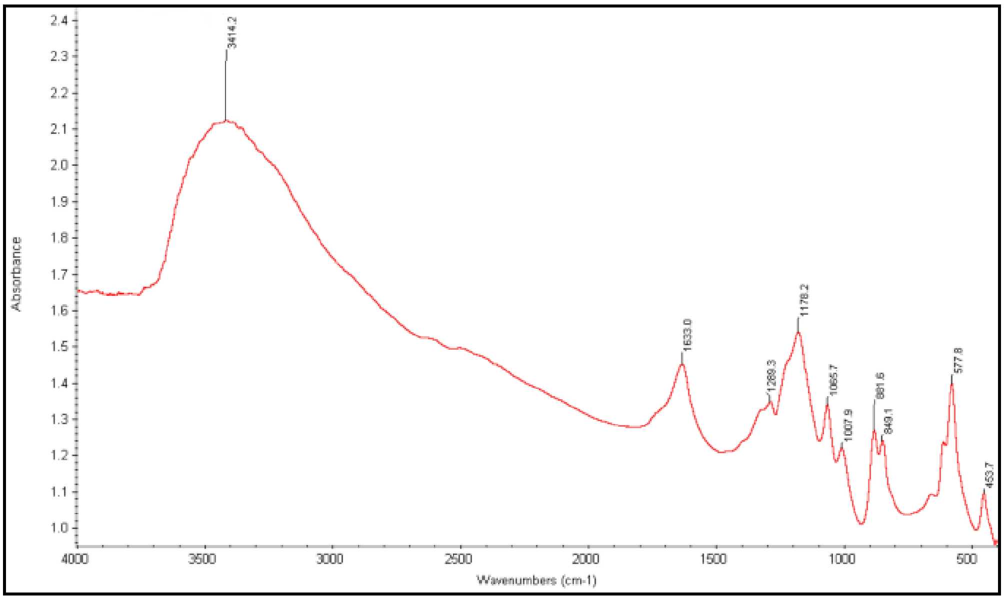

Fig. 5. FTIR Spectrophotometer analysis of Magnetite nanoparticles synthesized from $FeCl_2$

Furthermore, broad absorption bands, due to C-O and C-OH vibrations characteristic of carbon compound, are observed in the 1065 and 1007 cm^{-1}. An intense absorption region beyond 580 cm^{-1} associated with stretching and torsional vibration modes of magnetite can also be seen. Also, the 1269 cm^{-1} band could be assigned to the ferrophase complex vibrations. An intense band at 1633 cm^{-1} may be assigned to the deformation vibrations of water molecules trapped onto the magnetite colloidal particles.

The UV/visible absorption spectra for magnetite nanoparticles are shown in Fig. 6. The magnetite nanoparticles display a surface Plasmon resonance band at 417 nm. The surface plasmon resonance band of the magnetite nanoparticles shows a red-shift and broadening of the peak in the spectrum[26].

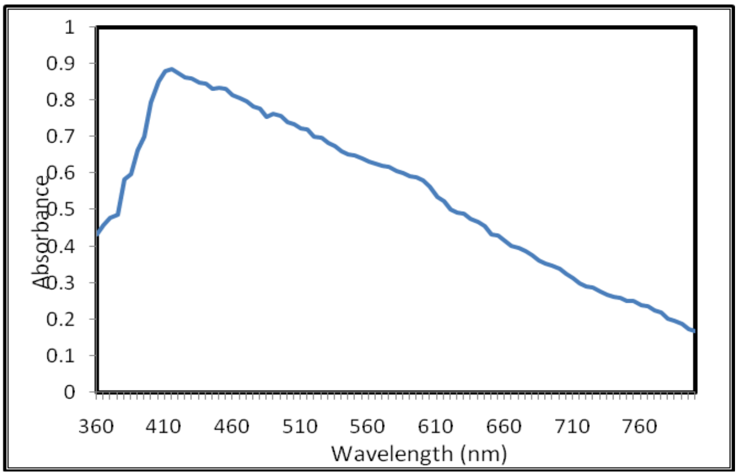

Fig.6. UV-Vis absorbance spectrum of Magnetite nanoparticles synthesized from $FeCl_2$

In terms of technology, the present leading alternative technique for removing arsenic from a ground water include co-precipitation, adsorption, membrane filtration, anion exchange, electro-coagulation, and reverse osmosis[27, 28]. Most of techniques used for removal of Arsenic from ground water, however, are not as effective as nano-magnetite, require large initial and maintenance costs, and are intensive labor since the affected area is very large[9]. In its nano-scale form, the most magnetic of all natural minerals, magnetite (Fe_3O), is effective in remediating arsenic[15, 29].

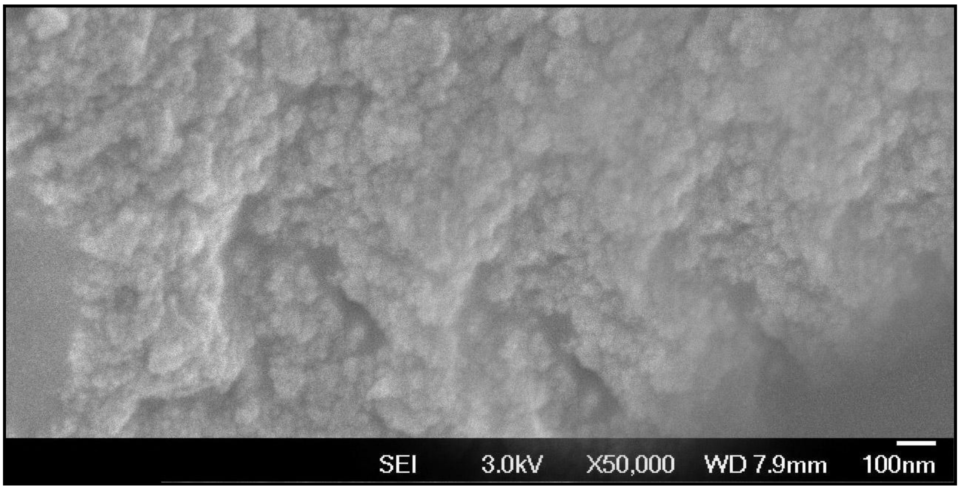

Fig. 7. Removal of Arsenic in the drinking water by Magnetite nanoparticles

The adsorption experiment was performed to find out the amount of arsenic removal by magnetite nanoparticles. It was found that as the removal efficiency of Arsenic from ground water by magnetite nanoparticles in highest adsorption of 95% was achieved.

After adsorption experiments the magnetic nanoparticles are collected and analyzed with SEM. It was found that the blockage of the pores showed that arsenic has occupied the space favoring the phenomenon of sorption (Fig. 7). SEM micrographs of magnetite nanoparticles after adsorption of Arsenic shows that of the surface areas of magnetite nanoparticles comprising of irregular shape and size of the nanoparticles are increased It will indicated that the adsorption of Arsenic by magnetite nanoparticles.

Conclusion

The magnetite nanoparticles ores are effective in removing arsenic from ground water. Nearly 95 % of arsenic was adsorbed from water using 4 g/L adsorbent dose at the optimum pH of 5.5. The results achieved in this research valuable for future studies for the treatment of groundwater for the removal of arsenic making the water safe for drinking purpose.

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