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Magnetite (Fe_3O_4) nanoparticles for chromium removal

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Abstract

Magnetite (Fe_3O_4) nanoparticles were synthesized by sol-gel method using ferric nitrate and ethylene glycol as precursors at 250ºC and 300ºC. X-ray diffraction (XRD) study was used to determine the particle size and structural properties. The microstructural and particle size analysis were carried out using scanning electron microscope (SEM). Magnetite (Fe_3O_4) nanoparticles were annealed at 250ºC obtained as smaller crystal size than that of 300ºC. Fourier Transform Infrared (FTIR) spectroscopy was used to identify the functional groups of active compound in synthesized magnetite nanoparticles and their corresponding bands were observed in the region between 500cm^{-1} and 4000cm^{-1} of infrared radiation. The observed peaks at wave number 574cm^{-1} and 424cm^{-1} due to the vibration of tetrahedral and octahedral sites which is indicative the formation of spinel structure of magnetite (Fe_3O_4). Removal of Cr was found 80% by the synthesized magnetite (Fe_3O_4) nanoparticles 25g/L at pH 4.0 and contact time was 250 minutes. The results showed that prepared magnetite (Fe_3O_4) nanoparticles can be used for the treatment of wastewater containing chromium.

Keywords: Magnetite; Nanoparticles; Sol-gel; Water treatment

Introduction

Magnetite is the first naturally occurring mineral of iron which was used by Greek about 6000 A. D. Although magnetite was the first naturally occurring magnet, there was no potential application of magnetite in the field of science and technology. Recently scientists and technologists of materials, environment and medical sciences have carried out various research and development activities on the possibilities of potential application of these materials. They have identified that these materials have numerous hidden characteristics possessing unlimited possibilities. So they are very much interested to synthesize of iron based magnetic nanoparticles and their application in the field of materials, environment and medical sciences.

In addition magnetic nanoparticles have superparamagnetic (Rahman *et al.*, 2012) properties, high chemical stabilities, easy synthesis processing and they are also biocompatible (Markides *et al.*, 2012) and lowtoxicity or cytotoxicity (Lei *et al.*, 2013). Because of super paramagnetic behavior magnetic nanoparticles offer zero coercivity andremanence (Lee, 2007). The magnetic structure of magnetite was first investigated by W. H. Bragg (Bragg, 1915) in England and Nishikawa (Nishikawa, 1915) in Japan. From the point of view of magnetic structure, magnetite is a typical inverse spinel structure in which Fe^{2+} and $Fe^{3+}$are disordered in the octahedral sites, while the tetrahedrons are fully occupied by Fe^{3+} cations and produce electric and magnetic properties due to hopping of electron between Fe^{2+} and Fe^{3+} in octahedral site (Verwey and Heayman, 1941).

The present work is interwoven in three disciplines; synthesis, characterizations and applications of magnetite nanoparticles in waste water treatment. method (Karami, 2010). Among these methods, sol-gel method offers some

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advantages such as good homogeneity, low cost, high purity, low temperature sintering, environmental friendly and also very much efficient (Kayani *et al.*, 2014).

On the other hand access to safe drinking water is very essential to protect human health. According to the guidelines for drinking water quality, globally at least two billion people use drinking water source contaminated with heavy metal or toxic minerals. It should be noted that total coliform, fecal coliform and E-coil are all indicators of drinking water quality. It is also reported by World Health Organization (WHO) that any drinking water should contain fecal and total coliform counts of 0, in any 10ml sample (WHO, 1996). If any bacteria or any heavy metal encountered in a sample, immediate investigative action should be taken for removal. The removal or inactivation or detoxification of bacteria, heavy metal or pathogenic is the last step in the treatment of waste water treatment.

There are some techniques for waste water treatment such as precipitation (Shen *et al.*, 2009), evaporation, solvent attraction, ion exchange, reverse osmosis, filtration (Hijnen *et al.*, 2010), adsorption (Klein*et al.*, 2013; Siraj *et al.*, 2012; Kabiraz *et al.*, 2016), coagulation (Katsoylannis and Zouboulis, 2006) and soon. Adsorption technique is one of the most important techniques for heavy metal removal from water. In this experiment magnetite (Fe_3O_4) nanoparticles have been used for heavy metal removal because of their high ratio surface to volume, resulting in a higher adsorption capacity for metal removal. In addition USA Food and Drug Administration has approved iron oxide nanoparticles (Fe_3O_4) for heavy metal removal (Dave and Chopda, 2014). The development of novel and cost effective magnetic nanomaterials is very indispensible for environmental remediation and pollution detection and these have been investigated intensively for these purpose.

In the present study, we focused on the synthesis of magnetite (Fe_3O_4) nanoparticlesby sol-gel method, characterization and water treatment containing chromium.

Materials and methods

Materials

All the chemicals were purchased from local market. The purity and specification of the chemicals were stated by the manufacturers and the chemicals were used in synthesis without further purification.

Preparation of magnetite (Fe_3O_4) nanoparticles

In order to synthesis magnetite nanoparticles 16.159 g of ferric nitrate ($Fe(NO_3)_3.9H_2O$) was dissolved in 25 ml of ethylene glycol ($C_2H_6O_2$). The solution was stirred and heated at 40^0C. Then the gel was heated at 80^0C until gel formation. Finally obtained gel was annealed at temperatures of 250^0C and 300^0C. The flowchart is as follows:

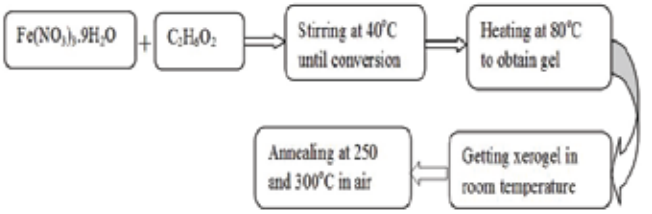

Fig. 1. Flowchart of synthesis technique of magnetite (Fe_3O_4)nanoparticles.

Fourier Transform Infrared (FTIR) analysis

FTIR spectra were recorded in the middleinfrared (4000 cm^{-1} to 400 cm^{-1}) on Shimadzu Prestige 21 with a resolution of 4cm^{-1} in the absorbance mode for 8 to 128 scans at room temperature.

X-ray diffraction (XRD)

XRD patterns of composite were recorded on Philips PWO4 Xpert pro X-raydiffractometer. The X-ray source was Cu-Kα with a voltage of 40kV and a current of 30mA. The measurement was in the scanning range of 5–70 at a scanning speed of 50s^{-1}.

Scanning Electron Microscope (SEM)

A HITACHI S-3400N, Japan (BSE) scanning electron microscope (VP-SEM) was usedto examine the microstructure of chitosan and composite without any coating to thesample surface and the image was taken at an accelerated voltage of 15.0kV.

Preparation of standard chromium (Cr) solution

50 ppm standard solutions of Cr was prepared for by appropriate dilution of a 1000 ppm of chromium (stand scharlau, spain) solution.

Removal efficiency (E) of adsorbent on chromium

25 g/L of magnetite (Fe_3O_4) nanoparticles was added to 50 ppm of Crsolution in polyethylene tubes. The metal solution was initially adjusted at pH 4.00 by adding 0.1M HCl or 0.1M NaOH. The tube was shaken well and centrifuged for 250 minutes. The result expressed as the removal efficiency (E) of the adsorbent on Cr, which is defined as

$$E (\%) = [(C_o - C_1) / C_o] \times 100$$

Where C_o and C_1 are the initial and equilibrium concentration of Cr solution (25mg/L), respectively. The Cr concentration was determined by atomic absorption spectrophotometer (Shimadzu AS7000).

Results and discussion

To apply magnetite (Fe_3O_4) nanoparticles for chromium removal, synthesis and characterizations of these nanoparticles have been carried out at two different temperature (250ºC and 300ºC) as well as their crystalline properties, nanosizeparticles conformation and their characteristic absorption bands of synthesized magnetite were studied.

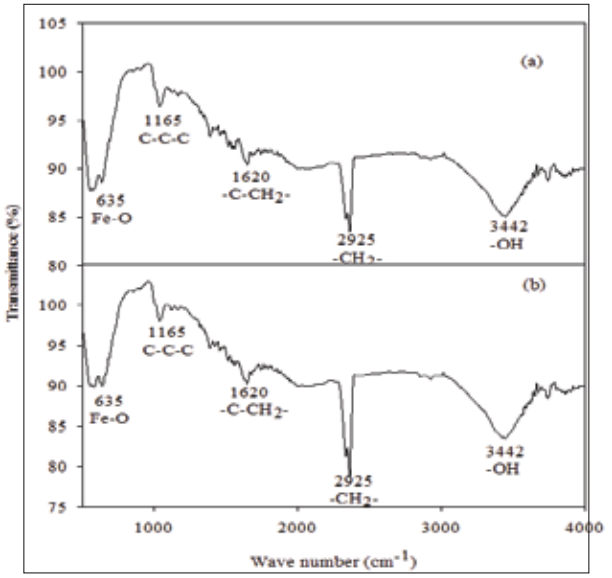

Fig. 2. FTIR spectra of the samples annealed at (a) 250°C and (b) 300°C

Fourier Transform Infrared (FTIR) analysis

Fig. 2 shows the FTIR spectra of Fe_3O_4 annealed at 250^{0}C and 300^{0}C. FTIR spectroscopy was used to identify the functional groups of the active components based on the peak value in the region between 500cm^{-1} and 4000cm^{-1} of infrared radiation. A broad absorption peak appeared at 3444cm^{-1} conferring the presence of moisture of O-H group in the sample. The characteristic peak below 1000cm^{-1} is due to the vibration of metal oxide. The peaks appearing below 700cm^{-1}are due tospinel structure. The band at around 500cm^{-1}is attributed to the intrinsic vibration of octahedral coordinated metal ions in the spinel structure conforming the spinel structure (Rahman *et al.*, 2015)of synthesized magnetic nanoparticles. These results are good agreement with the reported value (Vinosel *et al.*, 2014; Kanagesan *et al.*, 2013).

Scanning Electron Microscopy (SEM) analysis of synthesized magnetite

Fig. 3 shows the scanning electron microscopy images of samples synthesized at 250^{0}C and 300^{0}C. Scanning Electron Microscope (SEM:Hitachi-S3400N) was used to determine microstructure and particle size of these synthesized samples. From the SEM results it is seen that the synthesized nanoparticles are nearly spherical in shape with a narrow size distribution and severely agglomerated.

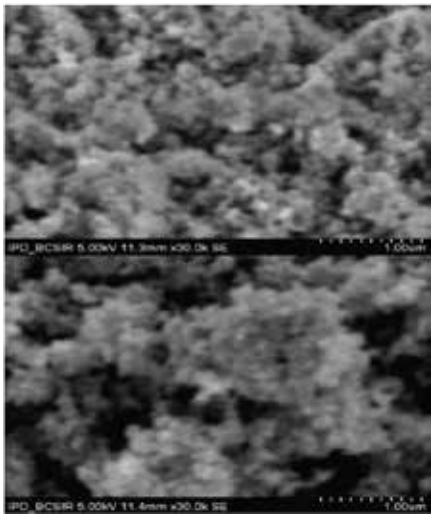

Fig. 3. SEM images of the samples annealed at (a) 250°C and (b) 300°C

X-ray Diffraction (XRD) analysis of synthesized of magnetite nanoparticles

Synthesized magnetite nanoparticles were characterized by X-ray diffraction system. In this system structural characterization was performed using Bruker D8 advance diffractometer employing with Cu-K_α radiation (1.54060Å)

at 30mA and 40kV. The XRD patterns of the synthesized magnetite nanoparticles are shown in fig. 4. The sample calcined at 250^{0}C shows diffraction peak at 2θ= 30^0,35^0, 45^0, 55^0, 58^0 and 65^0 are assigned to (220), (311), (400), (422), (511), (440) and (533) planes of cubic structure. Among the peaks the diffraction at an angle 2θ=35^0 could be attributed to Fe_3O_4, face centered cubic structure which is well matched with JCPDS card no. 85 1436/JCPDS card no. 19-0629. In the XRD patterns, there are no typical γ-Fe_3O_4 peaks such as (110), (210) and (211) on the other hand the synthesized samples are black in colour with crystalline size 18.46nm and 27.68nm. So it is significant that the synthesized particles mainly consist in magnetite nanoparticles. This result is also in conformation with the reported results (Shaker *et al.,* 2013; Wang *et al.,* 2013).

Cr removal capacity of charcoal, chitosan and prepared composite

The removal efficiency of chromium by magnetite (Fe_3O_4) nanoparticles at pH 4.0 with 250 minutes contact time and 25g/L dose was found 88%.

Table I. Crystal size and strain of synthesized magnetite

Sample	Crystal size	Crystal strain
Annealed at 250 ^{o}C	18.46	0.0064
Annealed at 300 ^{o}C	27.68	0.0043

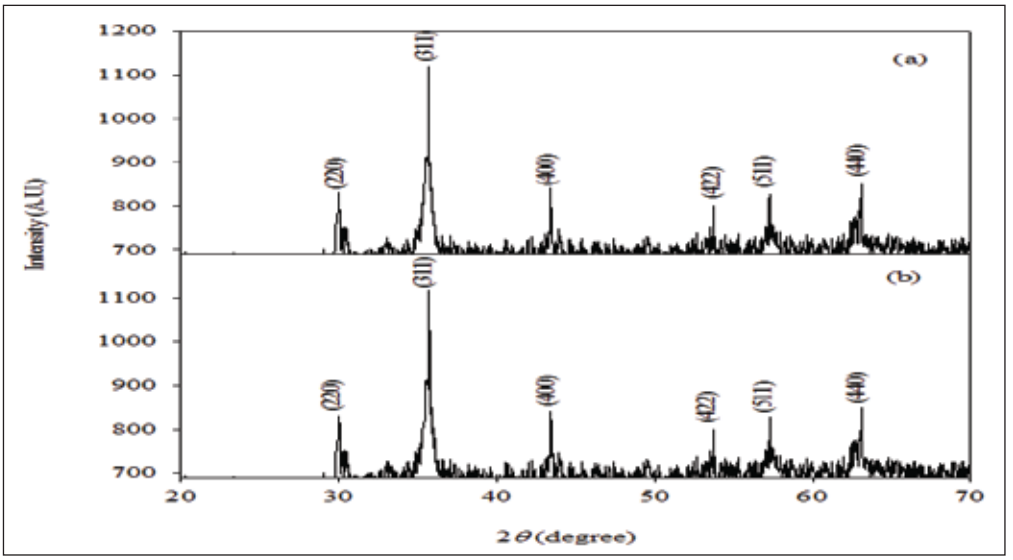

Fig. 4. XRD patterns of synthesized magnetite annealed at (a) 250^{o}C and (b) 300^{o}C

The crystalline size of the nanoparticles is also calculated by Scherrer formula, $D = \frac{k\lambda}{\beta cos\theta}$, where k is a dimensionless shape factor, λ is the x-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) and θ is the Bragg angle. Crystal size and crystal strain of the synthesized samples of magnetite (Fe_3O_4) nanoparticlesare shown in the Table I.

Conclusion

Although there are various physical and chemical methods of synthesis of magnetite (Fe_3O_4) nanoparticles, sol-gel method has been used in this study because of its simplicity and better control of particle size. The synthesized samples were characterized by XRD, FTIR and SEM. The FTIR results confirm the synthesized nanoparticles are in cubic structure of magnetite. From

XRD study it isseen that the diffraction peaks are consistent with the standard pattern of JCPDS card no. 85-1436/19-0629 and crystal size are in nano range. From the SEM results it is seen that the synthesized nanoparticles are nearly spherical in shape with narrow size distribution and severely agglomerated. Further mechanistic details of synthesis of magnetite (Fe_3O_4) nanoparticles and their removal of heavy metals from wastewater are being explored at different condition in our laboratory and will be reported in due course.

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