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Removal of Lead (II) Ions from Water by Using Green Nanotrimanganese Tetroxide

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Abstract

Inorganic pollutants like heavy metal ions and organic pollutants like pesticides and dyes are the main causes of water pollution. These contaminants cause serious issues for the environment and public health when they are present. To get rid of these contaminants from water bodies, several methods are employed.Due to its ease of use, great efficiency, abundance of adsorbents, and low sludge creation, adsorption is the most advantageous method for purifying water.Therefore, using an external magnetic field to remove magnetic nanomaterials from solution can be a potential approach.The scientificcommunity is veryinterested in magneticnanoparticles as an adsorbent for treating contaminatedwater.The current studylooks onthe efficient removal of lead (II) ions from waste water using green produced Mn_3O_4 nanoparticles.A straightforward, nontoxic, environmentally acceptable,and economicalgreen technique was used to create Mn_3O_4 nanoparticles by mixing an aqueous extract of Simarouba glauca plant leaves with a solution of manganese (II) acetate.PXRD, FT-IR, UV,SEM and TEMwere used to analyze the produced nanoparticles. These findings demonstrated that the Mn_3O_4 nanoparticles that were produced had a tetragonal hausmannite spinel structure and were spherical in shape. The produced Mn_3O_4 nanoparticle is an effective adsorbent for the removal of heavy metal ions and for the purification of waste water, according to adsorption studies conducted on lead (II) ions.

Keywords: Adsorption, Greensynthesis, Hausmannite, Mn_3O_4, Spinel

INTRODUCTION

Applications for magnetic nanoparticles are numerous and include drug administration, data storage, energy generation, magnetic resonance imaging (MRI), and environmental remediation [1–5]. Water pollution is mainly due to organic pollutants like dyes, pesticides etc and inorganic pollutants like heavy metal ions. The removal of heavy metal ions from waste water has been accomplished through the development and use of numerous technologies and techniques. These techniques aim to lessen the detrimental effects that heavy metals have on ecosystems and human health by bringing their concentration down to levels that are tolerable. Among the easily accessible methods include coagulation, ion exchange, solvent extraction, flocculation, chemical precipitation, adsorption, membrane filtration, electrochemical processes, and phytoremediation [6, 7]. The important methods to remove ions from water are ion exchange, membrane separation, adsorption, chemical precipitation, reverse osmosis, coagulation and flocculation and electrodeionization. Adsorption is a most favorable process for water purification due to its simplicity, high efficiency, availability of numerous adsorbents and less sludge generation [6]. In comparison to other wastewater treatment technologies, adsorption is thought to be a more effective and economical way to remove heavy

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metals from wastewater. The creation of an excellent effluent is the primary benefit of this process. Since adsorption is a cost-effective technique for heavy metal remediation, it has an advantage over other methods. Most of the time, the adsorbent may be recycled and utilized again. Adsorption is an environmentally benign process because it is simple to use and produces no harmful pollutants. The distribution of functional groups, large surface area and porosity, polarity, and cost-effectiveness are important considerations when choosing adsorbents. The chemical methods used to remove ions responsible for hard water are ion exchange, lime softening and soda process. A large number of adsorbents like chitosan and its composites, activated carbon derived from different waste materials, single/multiwall carbon nanotubes, nanoscale metal oxides, cellulose and its composites, graphene and its composites have been used efficiently for removal of heavy metal ions in recent years [8.9]. However, many of these adsorbents required the use of next separation process, which in turn increases the operational cost. Hence, magnetic nano-materials can be a promising material to be easily separated from solution through an external magnetic field. Magnetic nanoparticles have generated an extremely large interest in scientific world as adsorbent for treatment of polluted water [10, 11].

Mn_3O_4 is one of the most stable manganese oxides with spinel structure and shows room temperature paramagnetic behavior. Mn_3O_4 nanoparticles of various size and morphologies are synthesized by a number of methods like sol-gel technique [12], co-precipitation [13], solvothermal/hydrothermal synthesis [14], microwave method [15], thermal decomposition [16] and surfactant assisted method [17]. However, the synthesis process is hazardous to the environment since these procedures involve poisonous raw chemicals, expensive conditions, or both. Because of this, environmentally friendly materials that also serve as reducing, capping, and stabilizing agents are being developed as a substitute for the frequently used, sometimes extremely hazardous, materials as precursors, reducing agents, and stabilizing agents [18–20].

In the present work trimanganese tetroxide nanoparticles (TMTN) were synthesised by green method. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, and powder X-ray diffraction technique (XRD) were used to analyze the generated TMTN. Waste water was treated with lead (II) by utilizing the prepared TMTN. The effects of a number of variables, such as the solution's pH, the dosage of the adsorbent, and the adsorbate's initial concentration, have been studied.

MATERIALS AND METHODS

Materials

All of the compounds used were of analytical quality, and no further purification was required.Manganese (II) acetate tetra hydrate [$(CH_3COO)_2Mn.4H_2O$] was purchased from Merck.

Methods

Preparation of Leaf extract

The leaves of Simarouba glauca were collected, cleaned, dried in the shade, and ground into a powder.A definite amount of the pulverized leaf was heated with fixed volume of distilled water in a microwave oven at 100W for 30minutes. It was cooled, filtered and the filtrate collected.

Synthesis of Mn_3O_4 nanoparticle

60ml of the above obtained filtrate was added dropwise to 50ml of 0.1M Manganese acetate solution with stirring for 30minute and then heated in a microwave oven at 100W for 15 minutes. The solution was then cooled and the brown precipitate was separated by centrifuging, wash several times with distilled water and ethanol. Finally the precipitate was dried and calcined in a muffle furnace at 500^0C for 2 hour. The obtained product was labeled as TMTN.

Characterization of Mn_3O_4 nanoparticle

The structural identity and phase purity of the produced products were confirmed by powder X-ray diffraction technique (PXRD) of Bruker AXS D8 Advance model with Cu Kα radiation.By turning it into a pellet using KBr, the Thermo Nicolet Avatar 370 model's Fourier transform infrared (FT- IR)

was used to identify the functional groups. The UV-VISIBLE spectrophotometer of type Cary 5000 was used to record the absorption spectra of the powder sample at room temperature. X-ray photoelectron spectroscopy (XPS) was performed on a K-ALPHASXM Scanning X-microprobe by British VG Corporation with an Al cathode as the X-ray source. Surface morphology of the sampleswereanalyzed by SEM of JEOL Model JSM - 6390LV, elemental composition by EDX of model OXFORD XMX N and particle size and shape by TEM of JEOL/JEM 2100.

Investigation of Adsorption on Nano Mn_3O_4

The adsorption studies on the surface were carried out in a batch manner utilizing a 250 ml clean and dried stoppered conical flask containing 0.05gm of synthesized TMTN. The flask was then placed on a mechanical shaker at 160 rpm and a known concentration of 100 ml Pb^{2+} solution was added. The rate of adsorption of lead on TMTN after desired time intervals [30, 60, 90, 120, 150 min. etc.] was determined using atomic absorption spectroscopy model iCE 3000. The trials were conducted again with varying pH, dosages of adsorbent, and concentrations of heavy metal ions in the solution.

The adsorption capacity q and removal percentage are expressed as follows:

$$q = \frac{[C0-Ce]V}{W} \quad (1)$$

$$\text{Removal percentage} = \frac{(C0-Ce)100}{C0} \quad (2)$$

where W is the weight of the adsorbent [g], V is the volume of solution [L], and q is the adsorbent's adsorption capacity [mg.g-1]. The starting and equilibrium concentrations of the adsorbate in solution are Co [mgL-1] and Ce [mgL-1], respectively.

RESULTS AND DISCUSSION

Colour and appearance

TheTMTN was a coffee brown coloured fine powder.

Powder X- ray diffraction technique

XRD peaks give the phase purity, structural identity, crystalline nature and particle size of the obtained nanoparticle. The powder XRD spectrum of the synthesized product (Figure 1) was well matched with JCPDS Card No. 24-0734 and all diffraction peaks were indexed to the tetragonal hausmannitestructure.Debye – Scherer equation is used to calculate the size of the particle and is nearly about 15nm.No peaks from other phases are found, suggesting the high purity of synthesized TMTN. The Debye-Scherer equation is,

$$D = \frac{k\lambda}{\beta cos\theta} \quad (3)$$

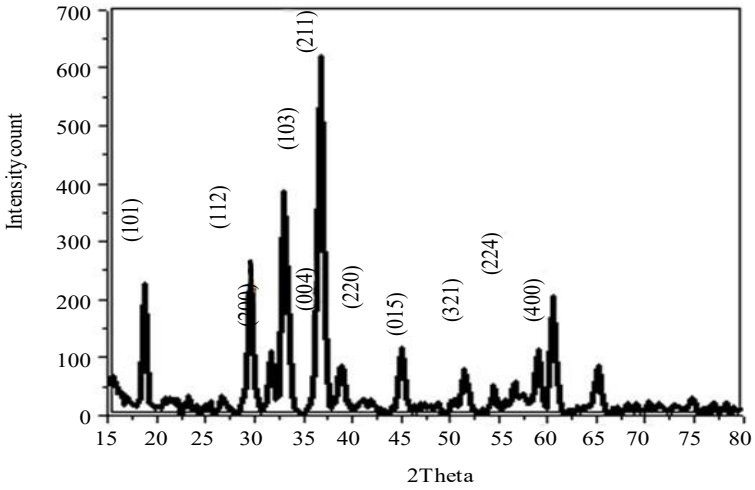

Figure 1. XRD pattern of TMTN.

where D- particle size, k – a constant(0.94), λ- wavelength of X- ray used, β – full width half maximum in radians and θ – Bragg's angle.

FT-IR spectroscopy

FT-IR spectrum of TMTN was used to identify the various bond types and functional groups present in it. IR spectrum of the sample is given in Figure 2. The broad band at 3436cm^{-1} was assigned to small amount of absorbed water in the Mn_3O_4 sample [21, 22]. The vibrational frequency at 625 cm^{-1} corresponds to the intrinsic stretching vibrations of metal at the tetrahedral site, M_{tetra}↔Owhere as the band stretching vibrations in the range 500-385 cm^{-1} account for octahedral metal stretching, M_{Octa} ↔ O [23, 24]. The peaks in the range 1084-1554 cm $^{-1}$ie, 1110cm^{-1} corresponds to the vibration of O – H bonds connected with Mn atoms [21]. The strong peak at 625 cm-1 is characteristic of hausmannite with a spinel structure, corresponding to the Mn-O stretching vibration of divalent 'Mn' ions in the tetrahedral co-ordination. The other strong peak at 492 cm $^{-1}$ corresponds to the Mn - O stretching vibration of Mn^{3+} ions in the octahedral co-ordination.

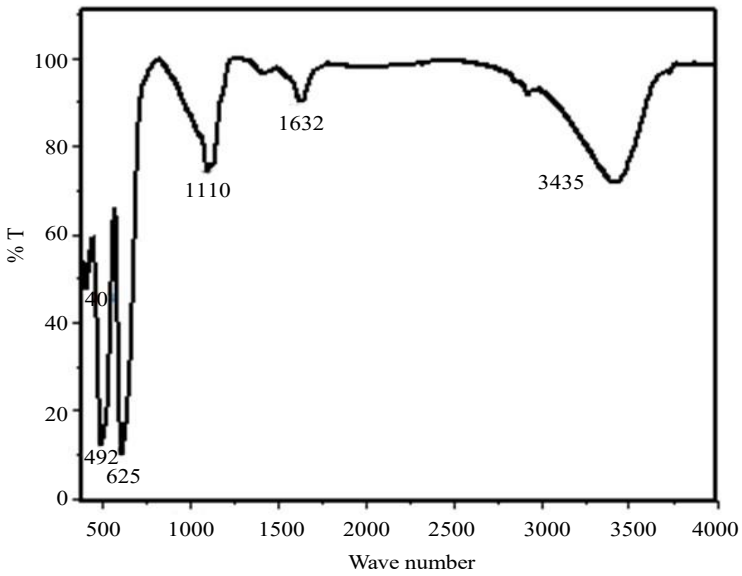

Figure 2. FT-IR spectrum of TMTN

UV-Visible Spectroscopy

UV-Visible absorption spectrum is used to find the allowed transitions in TMTN .The UV-Visible spectrum is given in Figure 3. The absorption bands at 226 and 353 nm are attributed to the allowed $O^{2-} \rightarrow Mn^{2+}$ and $O^{2-} \rightarrow Mn^{3+}$ charge transfer transition respectively [25,26].This spectrum is typical of the hausmannite phase.

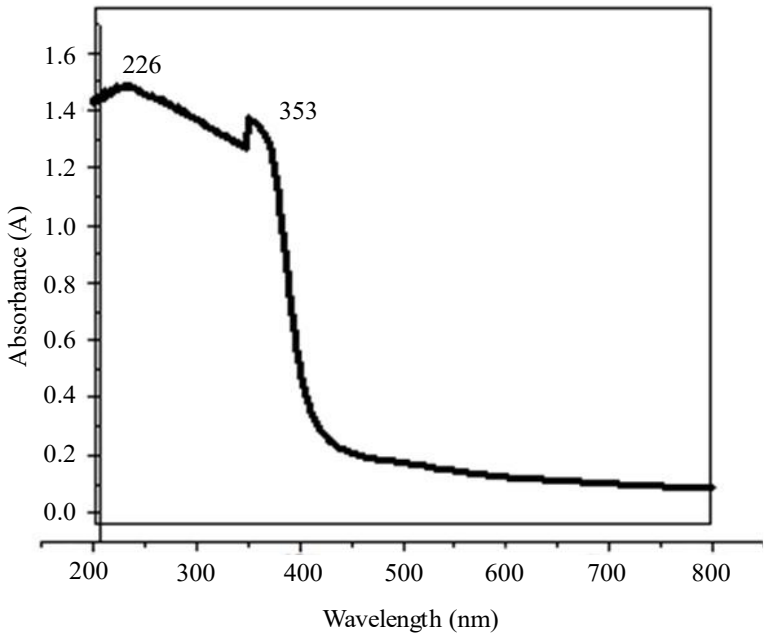

Figure 3. UV-Visible spectrum of TMTN.

SEM Image

The SEM image (Figure 4) shows well-defined morphology and a nearly spherical shape for the prepared Mn_3O_4 nanoparticle. The EDX spectrum (Figure 5) shows that the prepared compound contains only Mn and O as elements. It is also confirmed from the Table.1.

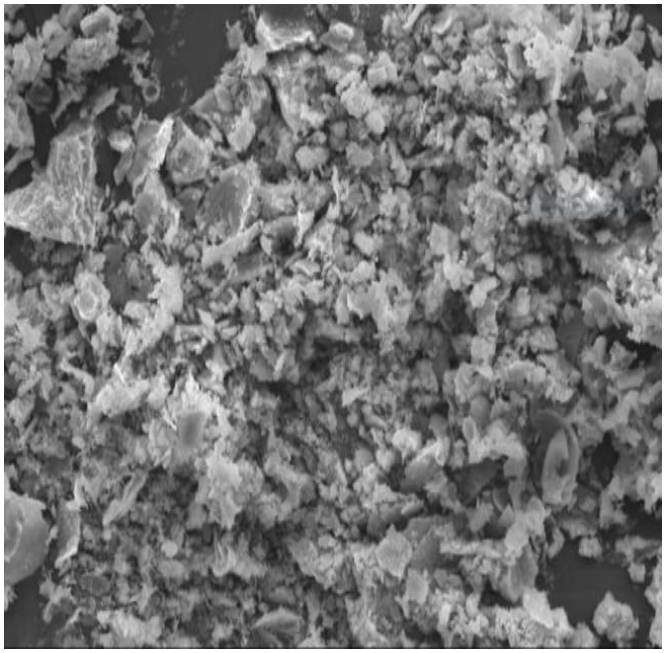

Figure 4.SEM images of TMTN

Table 1. Elemental composition of TMTN.

Element	Weight %	Atomic %
O	22.14	49.41
Mn	77.86	50.59
Total	100	100

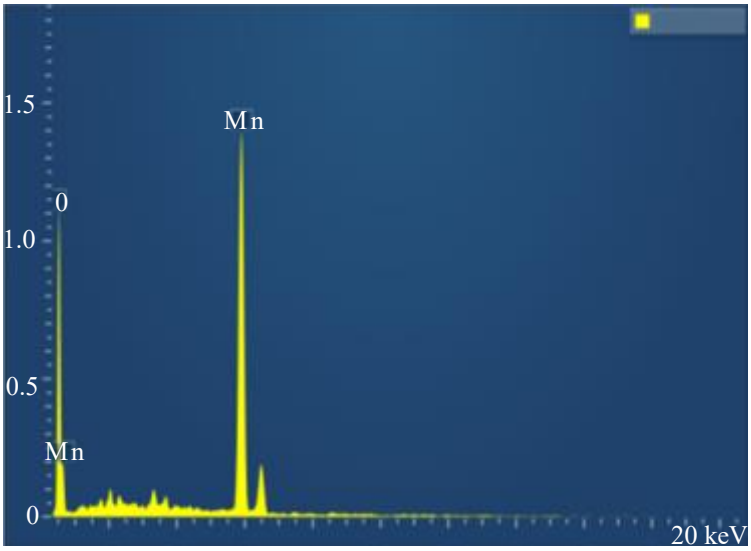

Figure 5. EDX spectrum of TMTN.

TEM image

According to the TEM image in Figure 6, TMTN has a spherical shape and homogeneous morphology with particles less than 20 nm. The selected area electron diffraction (SAED) pattern in Figure 7 indicates that the particles are clearly crystalline. The hausmannite structure of the produced TMTN is further demonstrated by the matching peaks in the XRD pattern and the diffraction rings on the SAED image.

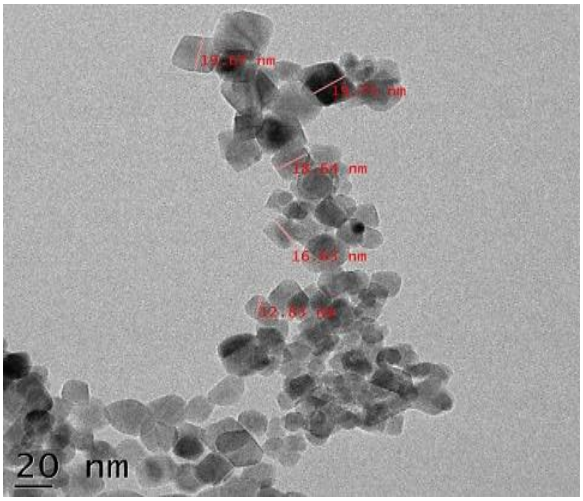

Figure 6. TEM image of TMTN

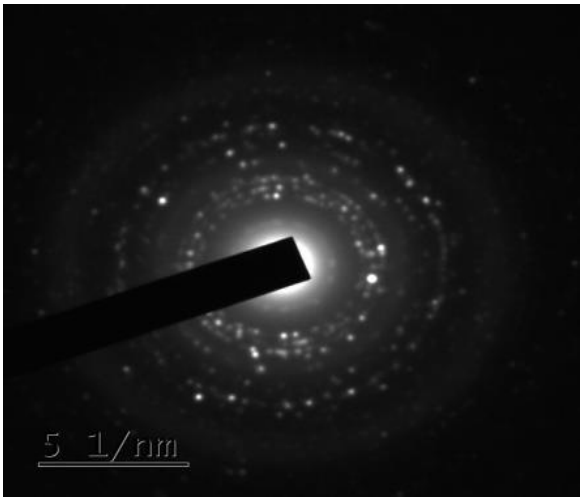

Figure 7. SAED pattern of TMTN

Adsorption of Lead (II) Ions in Solution

A small portion of the Pb (II) solution was withdrawn at regular intervals from batch method and absorbance was measured by Atomic Absorption Spectroscopy. It was noted that the absorbance of the solution decreased with increasing time intervals.

Influence of Concentration of Lead (II) Ions

The effect of adsorbate concentration on the rate of adsorption was studied by varying the concentration of Pb (II) ions from 10 to 40 ppm (Figure 8). As the concentration increases, the rate of adsorption reduces, reaching a maximum at 10 ppm. At low concentrations, the ratio of surface active sites to total metal ions in solution was high. After then, every metal ion in the solution was eliminated

due to their interactions with the adsorbent. However, at high concentrations, there was little metal ion absorbed per unit weight of adsorbent and a steeper concentration gradient.

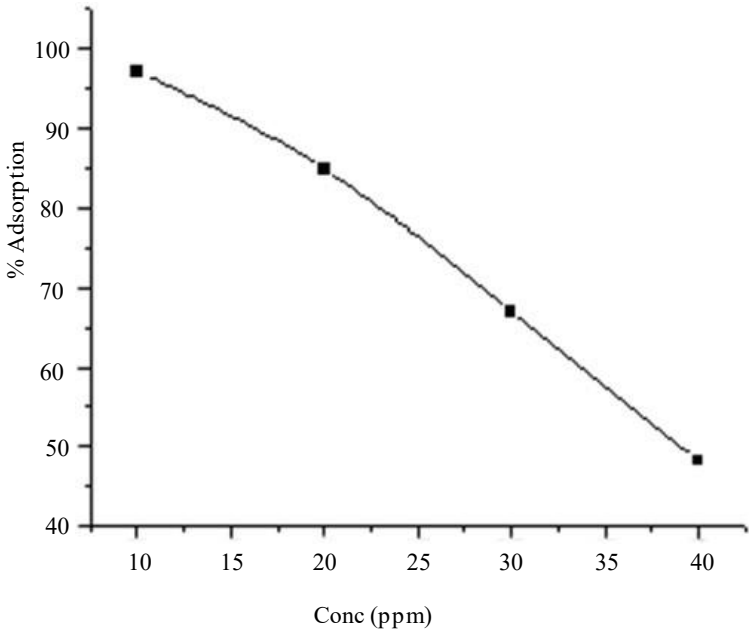

Figure 8. Effect of initial Conc. of Pb (II) ions.

Effect of Adsorbent Dose

The rate of adsorption was examined by varying amount of adsorbent from 0.025 to 0.1 gm/100ml of 10ppm Lead solution (Figure 9). It was observed that the rate of adsorption increases rapidly with time on increasing the amount of adsorbent up to 0.05gm. But at higher dose (0.075 to 0.1gm), greater is the availability of exchangeable sites for the ions. But the increase in dosage beyond a certain level results in no further increase in adsorption, may be due to the fact that the amount of ions bound to the adsorbent and the amount of free ions in the solution remains constant [27].

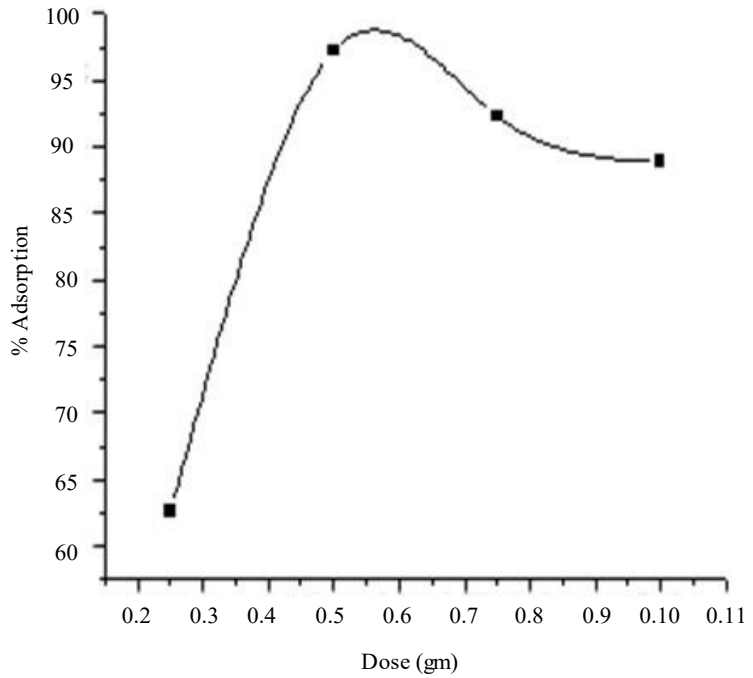

Figure 9. Effect of adsorbent dose.

Influence of pH

The pH of the solution affects how well the adsorbent is removed from it (Figure 10). The ionization state of the sorbent's functional groups, which influences the availability of binding sites, and the metal chemistry in solution are both factors that influence how pH affects metal adsorption [28, 29]. The form of the hydroxyl groups covering the metal oxide surface in the aqueous phase changes with changing pH levels [30]. The way that hydrogen ion and counter-ion activity behave in an aqueous solution explains how adsorptivity varies with pH. Up to pH 6, the hydrogen ion activity falls while the percentage adsorptivity rises. Since the concentration of hydrogen ions is too low and precipitation occurs in strong basic pH, adsorptivity falls above pH 6 [31].

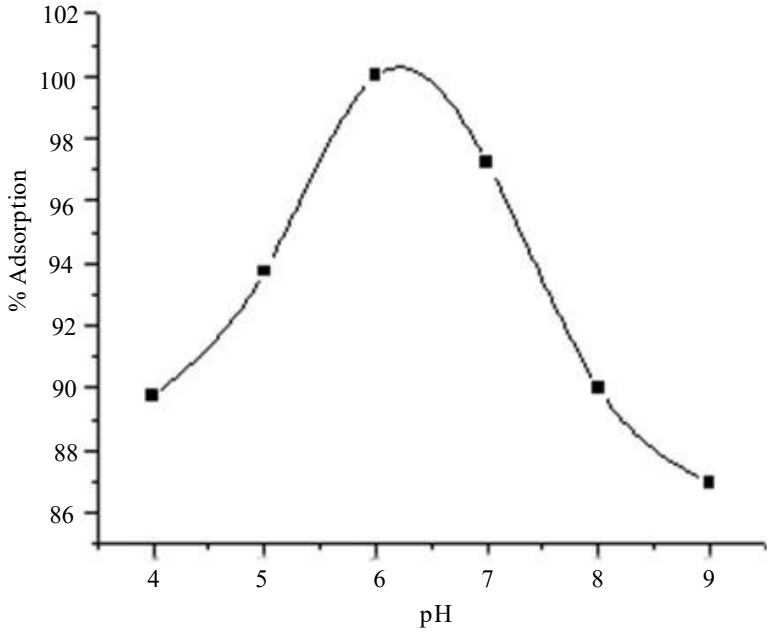

Figure 10. Effect of pH on adsorption.

CONCLUSIONS

Synthesis of pure Mn_3O_4 nanoparticles in a simple, eco-friendly, non-toxic and environmentally efficient green method from *Simarouba Glauca* leaf extract. In the synthesis of TMTN, an aqueous extract of Simarouba glauca leaves has been employed as a capping agent as well as a reducing agent. The Mn_3O_4 nanoparticle synthesized by this method has tetragonal hausmannite spinel structure with sphere like morphology and having particle size 15nm. Lead (II) ions in the current experiment might be adsorbed from solution using TMTN. The optimum reaction conditions of percentage adsorption with nano Mn_3O_4 were experimentally determined. It was found that lead (II) ion concentration of 10ppm, adsorbent dose of 0.05gm and pH of 6 are the optimum conditions for Lead (II) ions in water. The synthesized Mn_3O_4 nanoparticle may be used for the removal of other inorganic pollutant from water.

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