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SYNTHESIS, CHARACTERIZATION OF IRON OXIDE (α-Fe_2O_3)NANOPARTICLES AND ITS APPLICATION IN PHOTOCATALYTIC REDUCTION OF CHROMIUM (VI)

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ABSTRACT

Synthesis of α-Fe_2O_3 Nanoparticles was successfully done by the Sol-Gel method and the powder was calcinated at 400^0. Synthesized particles were characterized by using SEM, XRD, FTIR, EDX. It was found that Hematite (α-Fe_2O_3) had a crystalline size of 11.55nm which was confirmed by XRD. The Hematite(α-Fe_2O_3) was compared with spectra against the Joint Committee on Powder Diffraction Standards Database(JCPDS) and SEM morphology which indicated that IronOxide Nanoparticles were of flower shape at higher magnifications. The FTIR showed the bonds between functional groups and the Fe-O group, O-H bending and vibration bonds. The presence of FeO, Fe, C, in nanomaterial was confirmed by EDX . The iron oxideparticles, α-Fe_2O_3 (Hematite) of crystalline size 11.55nm were used in the study of photocatalytic reduction of Chromium (VI). Various parameters like Metal concentration, Dosage of Nanoparticles, Contact time and pH were studied. pH maintained for the solutions of different concentrations were 4,5,6,7 and 10.The concentration of Chromium (VI) solution taken for the study was 2,4,6,8 and 10ppm. Keeping concentration and dosage constant, pH was varied. Then concentration was varied by keeping dosage and pH constant. Later, dosage was varied by keeping concentration and pH constant. Dosage of iron oxide taken was 50mg, 75mg, 100mg, 125 mg and 150mg. It was observed that photocatalytic reduction by Iron oxide nanoparticles (IONP) was more effective at metal concentration 2ppm, IONP dosage 100mg, pH 4, and contact time of 150 min with 96.09% reduction of Chromium (VI).

Keywords: Iron Oxide Nanoparticles, X-ray diffraction, Scanning Electron Microscope, EDX, FTIR, Chromium(VI) , UV-Vis Spectrophotometry, Photocatalytic reduction

INTRODUCTION

Heavy metals are very toxic to living organisms. The presence of heavy metals at very low levels too will cause ill effects to the living beings. It has been a major concern about the presence of pollutants and many toxic heavy metals in water.With so many heavy metal ions present in industrial wastewater, Chromium (VI) is one of the dangerous heavy metal which is carcinogenic and toxic.[1]The presence of Chromium (VI) in water may be from many activities of the industries and through agricultural practices. Many industries like chrome plating, timber and leather tanning, metallurgical alloying, electronic, ceramics, pigment manufacturing,textile, etc. where industries release Cr(VI) in effluent streams. Such effluents must be treated to convert it to the less toxic trivalent form before discharging into the sewer.[2] Chromium(VI) is potentially toxic to humans and aquatic life, causing an oxygen demand in receiving waters, and impart taste and odor to drinking water. Heavy metals in high levels poses serious health problems in human and animals; in extreme cases it causes death.

Cr (VI) is five hundred times more toxic than Cr (III).[3]If chromium is accumulated in the lungs, it causes pulmonary sensitization. Many other influences of human exposure to chromium are: dermatitis, renal tubular damage, liver abnormalities, skin irritation and scaling, irritation to gastrointestinal mucosal tissue and hematological toxicity.[4] And Chromium (VI) compounds induce DNA damage, gene mutation, and chromosomal aberration in a number of targets.[5]Consequently, the need for heavy metal removal has become a must. According to Indian standards, the permissible limits for chromium is 0.05 mg/l.[6] There are many methods for treating heavy metals, such as electroplating, evaporating, chemical precipitation,

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flotation, membrane filtration, oxidation, reduction, ion exchange and adsorption[7,8]but they have their limitations.

Photoreduction is one of the techniques for remediation of heavy metals in effluents. Research on Oxidation of organic pollutants has been carried out in treating the effluent water containing heavy metals and even in domestic water.[9]The use of photocatalyst in reducing the toxicity of heavy metals is less explored.[10].The photocatalysis method has shown promising results in degrading pollutants or changing themselves to less toxic forms.[11, 12]There is a need for such technology to be used as the toxicity of an inorganic substance depends on their oxidation states.[13]The objective of this work is to reduce the heavy metal Cr(VI)from its toxic form to nontoxicstateCr(III) by using iron oxide as a photocatalyst.

EXPERIMENTAL

Chemical used

Potassium Dichromate, Sulphuric Acid, Sodium Hydroxide. All the Chemicals used were of analytical grade samples.

Equipment used

pHMeter, the photocatalytic Reactor, UV Visible Spectrometer.

Preparation of Chromium (VI) Stock Solution

2.828the 9 gm of Potassium dichromate was weighed and was diluted in 1000ml of distilled water in volumetric flask up to the mark to get a 1000ppm solution.Distilled water was used to prepare the solutions and analytical grade reagents were used. Synthetic samples of different concentrations of 2, 4, 6, 8 and 10 Chromium (VI) were prepared from this stock solution. The pH of the aqueous solution was brought to the desired value by adding 0.05N H_2SO_4 or 0.1 N NaOH solution.

Procedure for Reduction of Chromium (VI)

2, 4, 6, 8 and 10ppm solutions prepared were taken for U.V analysis to know the absorbance.The analysis for Chromium(VI) is done by using spectrophotometer after adding Diphenylcarbazide in acid solution.And the absorbance was used as reference.100ml of stock solution with predetermined Chromium (VI) concentration and pH was taken in a quartz tube. 100mg of iron oxide nanoparticles which were synthesized was added to the solution. Chromium (VI) solutions in quartz tubes were placed in a photocatalytic reactor, where the solution was exposed to a visible light source. After every 30minutes, 1ml of the sample was collected and the collected samples were centrifuged using microcentrifuge.A portion of the centrifuged sample was taken containing into a 100 ml beaker. It was made up to the volume to about 50 ml with water. pH of this solution was adjusted to 1.0 ± 0.3 using 0.2N H_2SO_4, and a pH meter. Transfer the sample into a 100 ml volumetric flask, and added 2.0 ml of diphenylcarbazide solution. The solution was diluted to 100 ml with water, mixed well.After 10 minutes the sample was taken for absorbance at 540 nm.The sample was taken for UV analysis to know the absorbance using reference solution.

Variation of Parameters:

pH maintained for the solutions of different concentrations were 4,5,6,7 and 10. The concentration of Chromium solution varied was 2, 4, 6, 8 and 10ppm.Keeping concentration and dosage constant, pH was varied. Then concentration was varied by keeping dosage and pH constant. Then dosage was varied by keeping concentration and pH constant. Dosage of iron oxide taken was 50 mg, 75mg, 100mg, 125 mg and 150mg.

RESULTS AND DISCUSSION

Characterization of Iron Oxide Nanoparticles

X-Ray Powder Diffraction

The obtained iron oxide nanoparticle was identified as α-Fe_2O_3 (Haematite) on comparison with obtained spectra against the Joint Committee on Powder Diffraction Standards Database (JCPDS). It was observed that, the intensity of the diffraction peaks of the samples increases with an increase in temperature and the

peak width at half maximum decreases, showing the crystallinity. The analyzed material is finely ground, homogenized, and average bulk composition is determined.[9, 11]

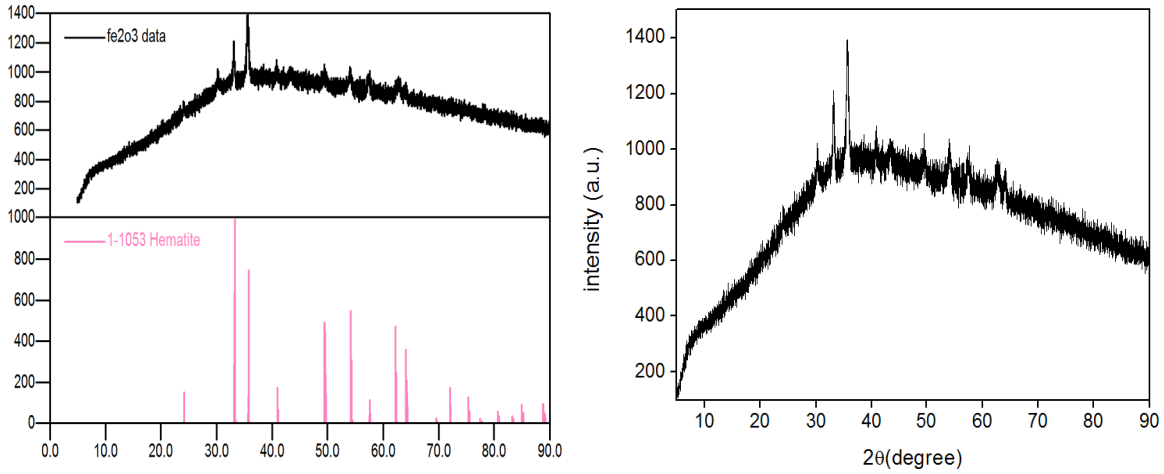


Fig.-1: XRD Graph for αFe_2O_3 Nanoparticles

Six characteristic peaks were obtained at 30.206°, 33.155°, 35.607°, 40.918°, 49.462° and 54.081° as per ASTM standard for α-Fe_2O_3 Nanoparticles.[15]
Particle size was calculated from Debye-Scherrer equation given by:

$$Dp = 0.94\lambda/\beta\cos\theta$$

Where, Dp = Particle size (in nm), β = Line broadening (in degrees) = 0.7714^0, θ = Bragg angle (in degrees) = 0.9521^0, λ = X-ray wavelength (in nm) = 0.154 nm
The particle size obtained was 11.55nm.

FTIR

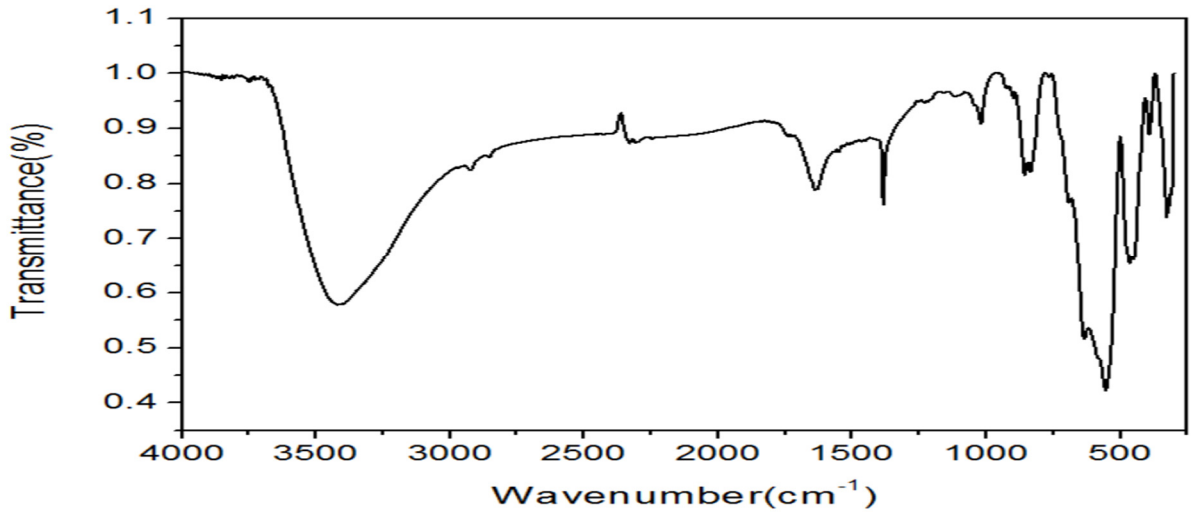


Fig.-2: FTIR Graph for α-Fe_2O_3 Nanoparticles

The Fourier Transform Infrared spectroscopy(FTIR) graph shows a broad region 3415 cm^{-1} and is called a stretching peak a sharp peak at 1634.3 cm^{-1} is called bending peak which is due to v(OH) and coordinated water δ(HOH).The peaks at 469.8 cm^{-1} and 555.7 cm^{-1} shows peaks of FeO[15].

Procedure

Nanoparticle powder sample was mixed with KBr powder and ground into fine powders & was pressed into pellets at 70psi. IR spectra were collected over the range of 400-4000$cm^{-1.}$

SEM Analysis

A scanning electron microscope (SEM) is a type of microscope that produces images of a sample by scanning it with a focused beam of electrons. Images show that particles range from 10-100 nm size and showed flowered type structure for nanoparticles.[15]

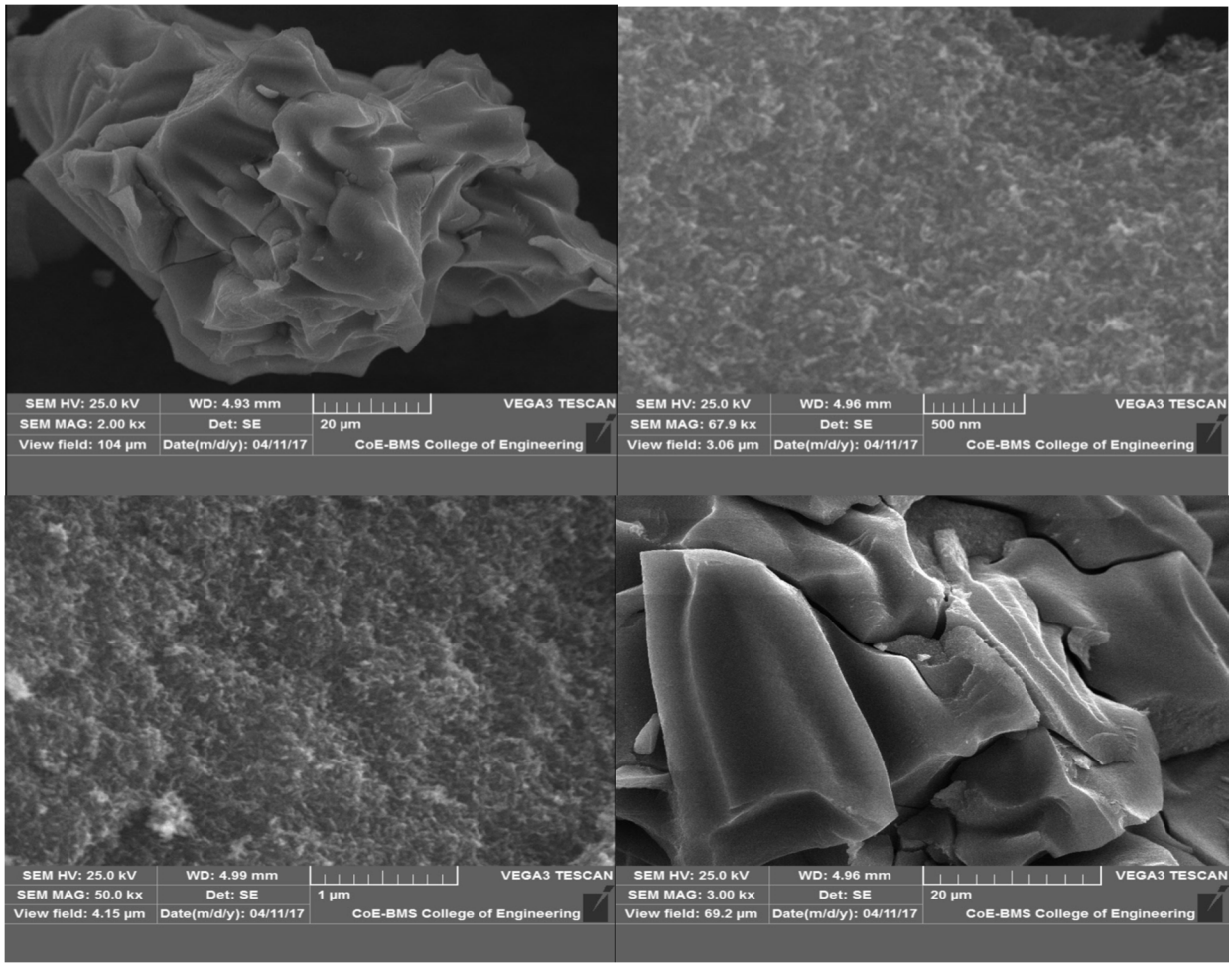
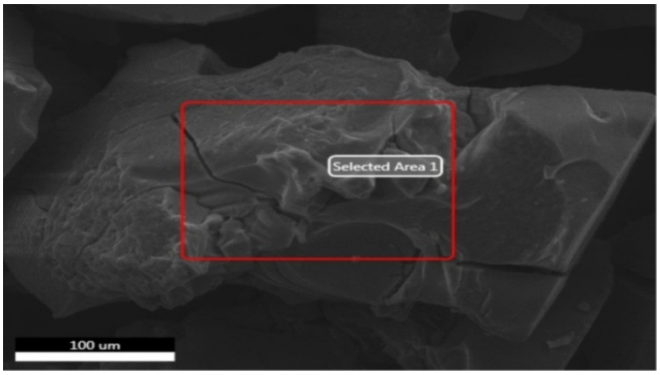


Fig.-3 SEM Images for α-Fe_2O_3 Nanoparticles

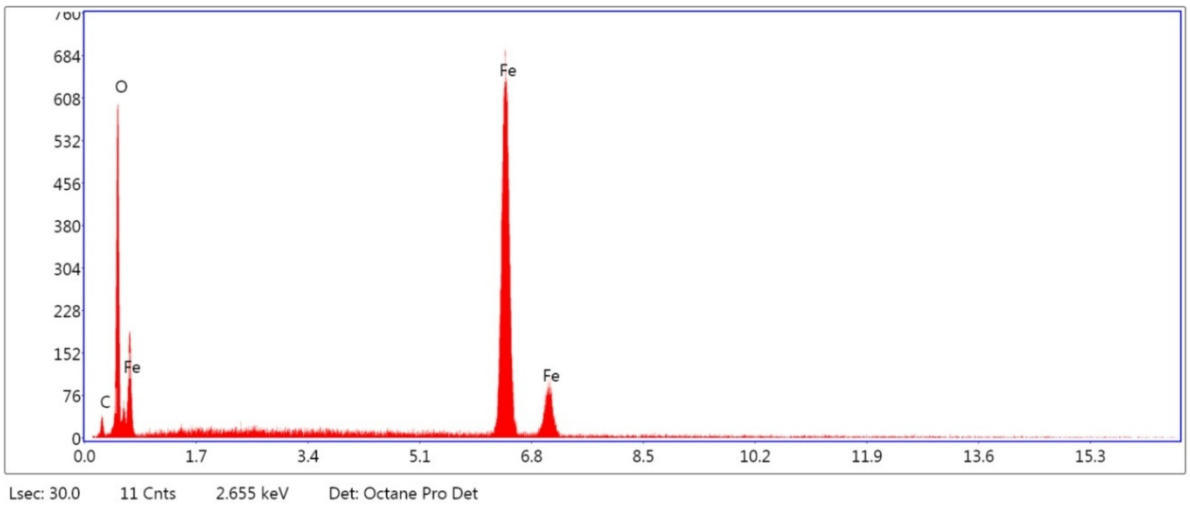
EDX

Energy-dispersive X-ray spectroscopy is a technique used for the elemental analysis or chemical characterization of a sample.EDX shows only the elements C, O, and Fe are present.[15]

Selected Area



(a)



(b)

Fig.-4: (a) EDX Image of IONP; (b) Graph of EDX
kV:25 , Mag :624, Time(S):30, Resolution(eV):123.3

Table-1

Element	Weight %	Atomic%	Net Int.	Error%	K ratio
CK	8.02	18.00	12.63	14.58	0.0243
OK	31.31	52.73	197.73	8.20	0.1386
FeK	60.67	29.27	620.92	2.15	0.5657

The chemistry behind the photocatalytic reduction is that, iron oxide nanoparticles having Fe^{2+} oxidation state converts to Fe^{3+} oxidation state.

$$3Fe^{2+} \xrightarrow{\text{Visible light}} 3Fe^{3+} + 3e$$

$$3e + Cr^{+6} \longrightarrow Cr^{+3}$$

During this conversion, it donates an electron to chromium heavy metal ions and chromium ion gets reduced to nontoxic form i.e. from Cr^{6+} to Cr^{3+} state. The reduction can be identified by UV visible spectrophotometer. For the photocatalytic reduction of chromium heavy metal, the photocatalytic reactor is used under visible spectrum. The photocatalytic reactor used was of 125 watts. Experiments were done on various parameters such as time, dosage, concentration and pH. Optimum results were found at which maximum reduction of Chromium took place.[13, 14]

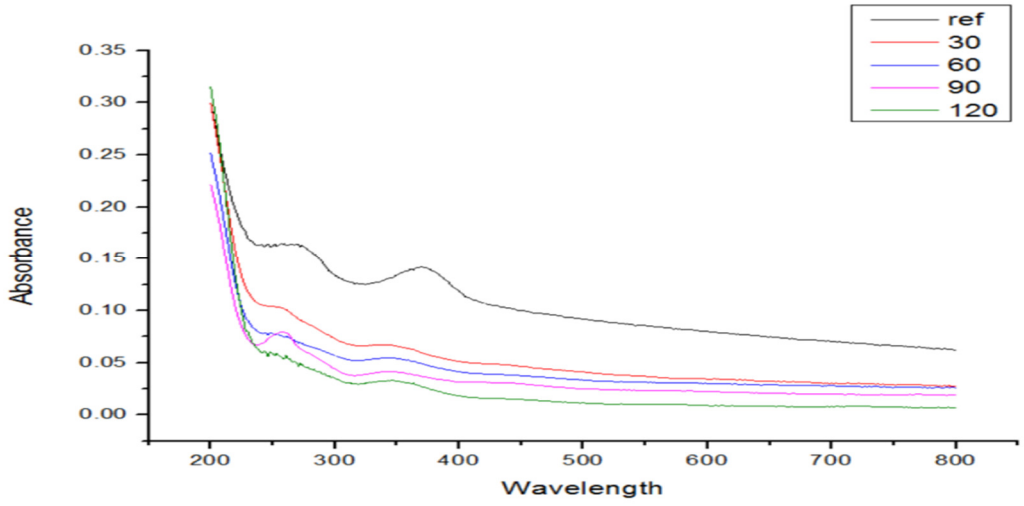


Fig.-5: UV-Vis Absorbance Graph (2ppm Conc., 4pH, 100mg Dosage)

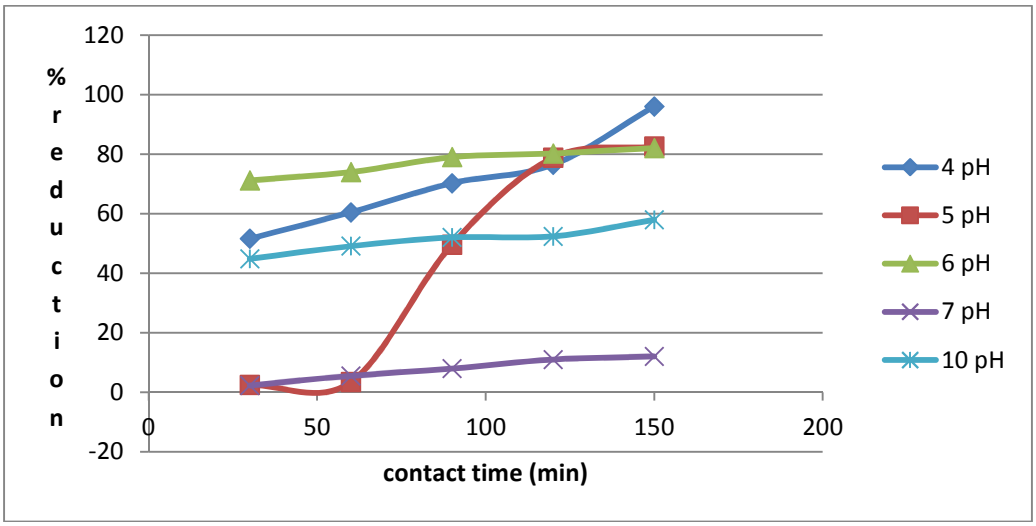


Fig.-6:% Reduction vs Contact Time at Dosage 100mg IONP and 2ppm Concentration for Different pH.

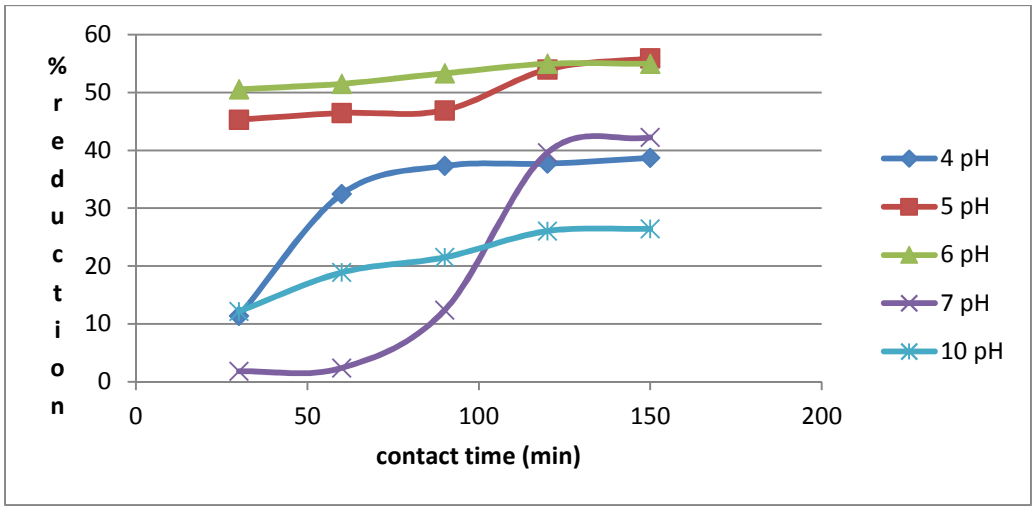


Fig.-7: % Reduction vs Contact Time at Dosage 100mg IONP and 4ppm Concentration for Different pH.

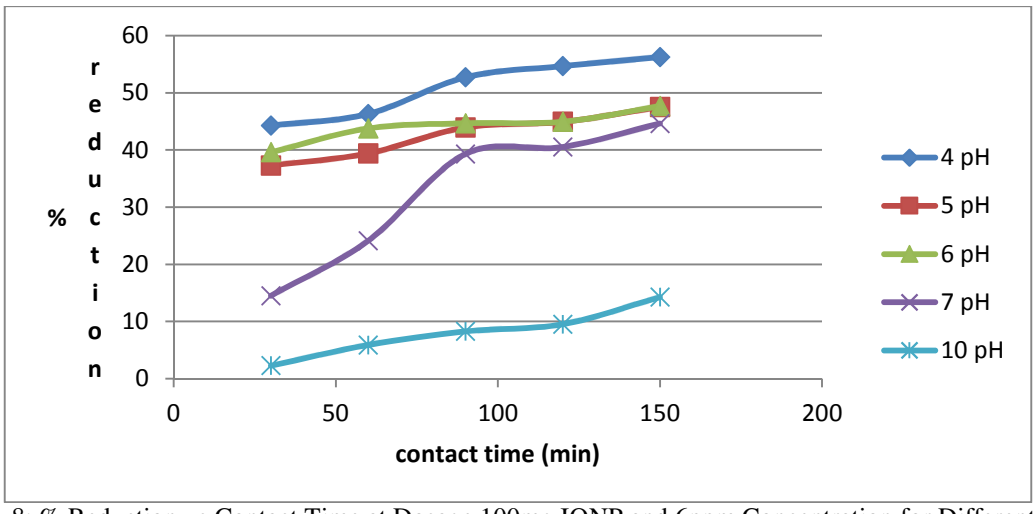


Fig.-8: % Reduction vs Contact Time at Dosage 100mg IONP and 6ppm Concentration for Different pH

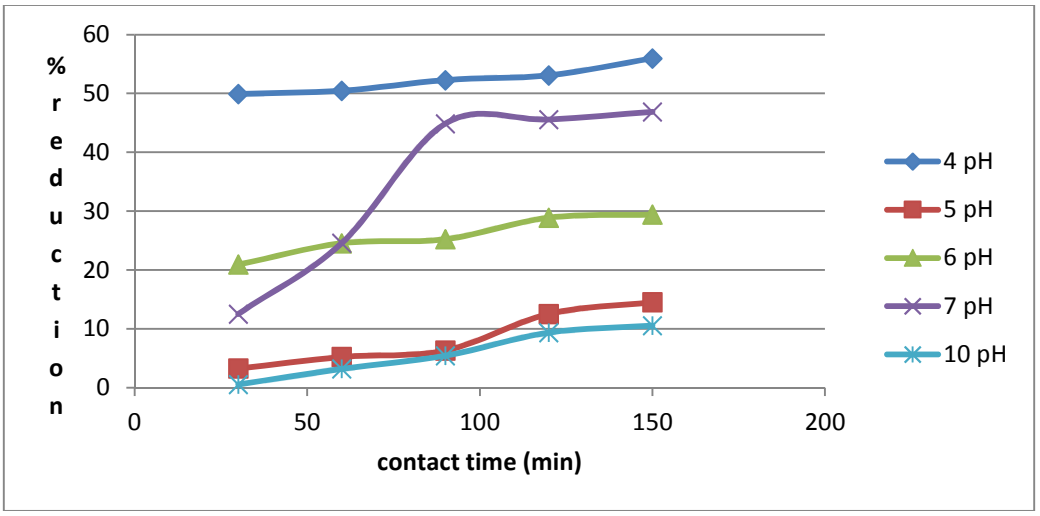


Fig.-9: % Reduction vs Contact Time at Dosage 100mg IONP and 8ppm Concentration for Different pH

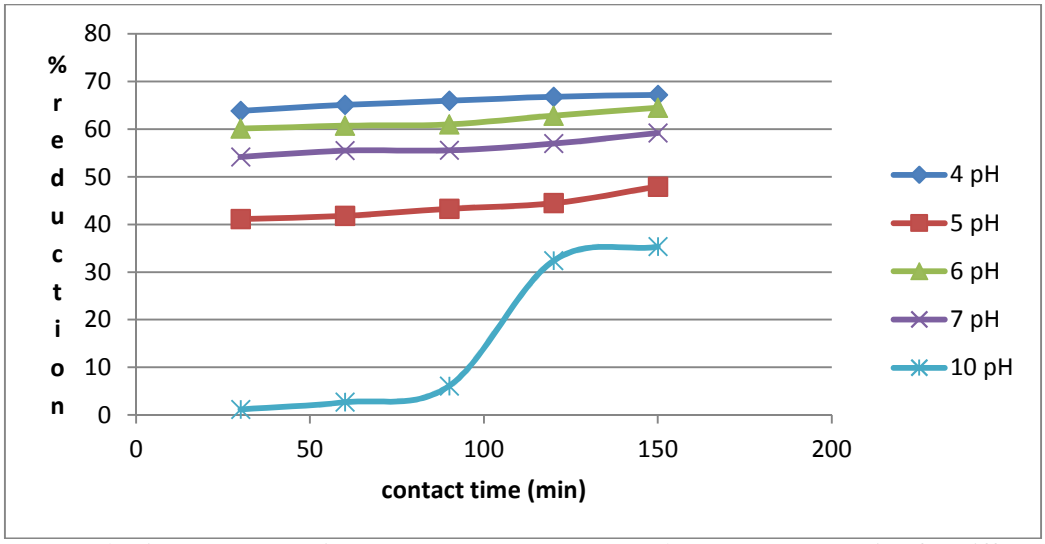


Fig.-10: % Reduction vs Contact Time at Dosage 100mg IONP and 10ppm Concentration for Different pH.

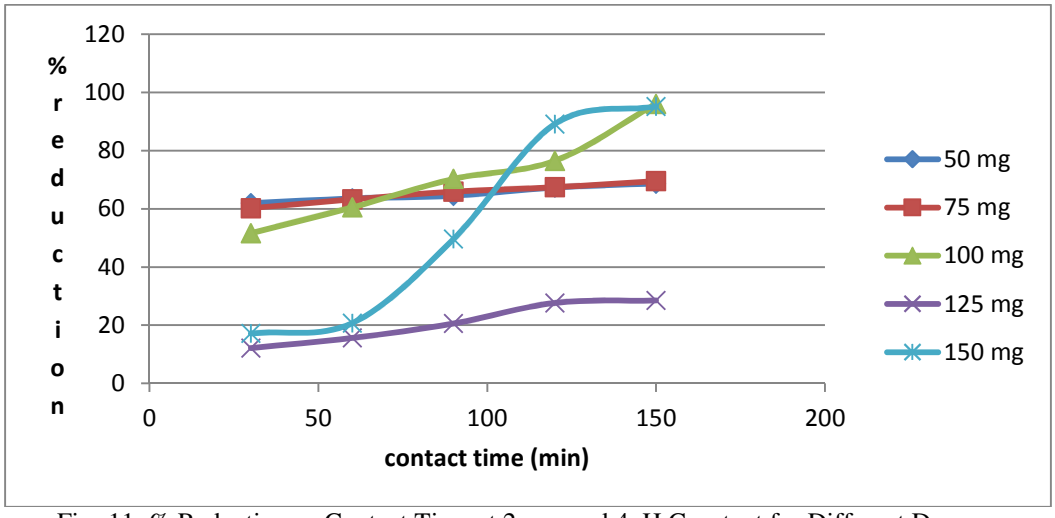


Fig.-11: % Reduction vs Contact Time at 2ppm and 4pH Constant for Different Dosage.

In the above Figures-6, 7, 8, 9 and 10 dosages was kept constant at 100mg and concentration 2ppm, 4ppm, 6pmm, 8pmm and 10ppm constant respectively with variation in pH. The highest reduction of 96.09%, 55.91%, 47.67%, 55.97% and 67.19% were found respectively. Therefore, it may be concluded that the maximum reduction was obtained at 4pH. Since, best results were found at 2ppm 4pH, dosage was varied (50, 75, 100, 125 and 150mg) as shown in Fig.-11. Best result was obtained at 2ppm metal concentration, 4pH and 100mg dosage of IONP with 96.09%reduction of Chromium (VI).

CONCLUSION

The iron oxide nanoparticles prepared by the Sol-Gel method was found to be hematite by XRD and flowered structured images were taken from SEM and the presence of iron oxide and functional groups were confirmed by FTIR. The size and shape were confirmed using SEM. Iron oxide (Fe_2O_3) Nanoparticles were synthesized and the particle size was found to be 11.5nm. The FTIR shows the bonds between functional groups and FeO group, H-O bending and vibration bonds. The presence of FeO, Fe, C, O in Nanoparticles was confirmed by EDX .Batch studies were conducted for the reduction of toxic Heavy metal Chromium (VI).In this work, Iron Oxide Nanoparticles were used as an effective photocatalyst for the reduction of Cr (VI) under UV-vis radiation (125 watts) source. The Nanoparticles with small crystalline size and strong visible-light absorption were appropriate for the photocatalytic reduction of Cr (VI). The effect of pH was investigated in reduction. The catalyst showed a high reduction in an acidic medium that is appropriate for the complete reduction at 4pH. Reduction increases with Contact time above 30min of UV-vis spectrum irradiation in acidic medium. The increase of Nanoparticles dosage beyond the optimum of 100mg resulted in the agglomeration of IONP, hence particle surface become unavailable for photoabsorption, and reduction. According to the results, maximum metal reduction Efficiency (%) for Cr (VI) was obtained at: pH=4; Contact time=150minutes; Fe_2O_3 dosage=100mg.

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