International Journal of Engineering & Technology, 7 (3.34) (2018) 388-393

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Synthesis, Characterization of Iron Oxide (A-Fe_2o_3) Nanoparticles and its Application in Photocatalytic Reduction of Cadmium (Ii)

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Abstract

The α-Fe2O3 Nanoparticles were successfully synthesized by Sol-Gel method and the powder was calcinated at 4000. SEM, XRD, FTIR, EDX studies were carried out for characterization. The XRD confirmed that nanoparticles were Hematite (α-Fe2O3) having crystalline size of 11.55nm which confirms the Hematite(α-Fe2O3) on comparison with obtained spectra against Joint Committee on Powder Diffraction Standards Database(JCPDS) and SEM morphology indicated that IronOxide Nanoparticles were of flower shape at higher magnifications . The FTIR showed the bonds between functional groups and Fe-O group, O-H bending and vibration bonds. The presence of FeO, Fe, C, in nanomaterial was confirmed by EDX . Synthesized iron oxide α-Fe2O3 (Hematite) crystalline size of 11.55nm was used in the study of photo catalytic reduction of Cadmium (II) .Different 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. Concentration of cadmium solution taken for the study were 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. It was observed that photo catalytic reduction by Iron oxide nanoparticles (IONP) was more effective at metal concentration 4ppm, IONP dosage 100mg, pH 5, and contact time of 150 min with 97.02% reduction of Cadmium (II).

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

1. Introduction

Nanomaterials have a wide range of applications, as in the technological and environmental challenges in the areas of solar energy conversion, catalysis, medicine, and water treatments. Several studies have addressed nanoparticles, mainly metal oxides, as effective and efficient adsorbents in the cleanup of environmental contaminants, mainly because nanoparticles can penetrate into the contamination zone where microparticles cannot.[1]Various adsorbents such as activated carbon, silica gel, and graphite oxide, iron oxide can be used in the purification of water. Among these adsorbents, iron-based magnetic nanomaterials have distinguished themselves by their unique properties, such as larger surface area-volume ratio, diminished consumption of chemicals, and no secondary pollutant. However, with another special property of this kind magnetic materials are realized and utilized in the context of environmental remediation.There are various techniques for the synthesis of iron oxide (haematite) nanoparticles of physical and chemical approaches, such as chemical precipitation, solvothermal, pulsed layer ablation , electro-spinning , hydrothermal , and sol-gel methods.[2] Among various chemical synthesis sol-gel process offers several advantages, including good homogeneity, low cost, and high purity.[3]

The sol gel process is a suitable wet route to the synthesis of nanostructured metal oxides. This process is based on the hydroxylation and condensation of molecular precursors in solution, originating a "sol" of nanometric particles. Further condensation and inorganic polymerization lead to a three dimensional metal oxide network denominated wet gel. Because these reactions are performed at room temperature, further heat treatments are needed to acquire the final crystalline state. Heavy metals are known to be toxic for living organisms even if they are present at low levels.[4] The presence of heavy metals and other pollutants in water continues to be a major concern.[5] Among different heavy metal ions present in industrial wastewater, Cadmium(II) is acutely carcinogenic and toxic. Cadmium (II) contamination may originate from various agricultural practices and chemical industries, including metallurgical alloying, ceramics, pigment manufacture, electroplating, and textile and such effluents must be treated to convert it to the less toxic form before discharging into the sewer.[6]

This heavy metals are potentially toxic to humans and aquatic life, create an oxygen demand in receiving waters, and impart taste and odour to drinking water.[7] Heavy metals in high levels possess serious health problems in humans and animals, in extreme cases can cause death.

Cadmium (II) is accumulated in the kidneys, the filtering mechanism is damaged resulting in the elimination of vital proteins and sugars from the body promoting kidney damage[8].

Some of the many other influences of human exposure to cadmium are; diarrhoea, bone fracture, damage to the central nervous system, damage to the immune system, and cancer development.According to Indian standards the permissible limits for cadmium is 0.003mg/l. There are various techniques for treating heavy metals in water and wastewater. Such as electroplating, evaporating, chemical precipitation, flotation, membrane filtration, oxidation, reduction, ion exchange and adsorption.

Photoreduction is one of the techniques for remediation of heavy metals in wastewater.[8] Oxidation of organic pollutants has been widely studied in connection with the treatment of drinking water and industrial water. However, the reducing capacity of photocatalyst, which can be profitably used, is less explored. The method has the advantage of destroying pollutants or transforming them into less toxic forms. This is an essential characteristic of photocatalytic technology for water treatment because the toxicity of inorganic substance depends on their oxidation states

2. Material and Methodology

2.1. Chemicals Used:

Synthesis of Iron Oxide Nanoparticles. Ferric Nitrate - $Fe(NO_3)_3{\cdot}9H_2O$
Ethylene glycol - $(CH_2OH)_2$
Synthesis and Characterization of Iron Oxide Nanoparticles
Reflux Condenser
Centrifuge
Hot Air Oven
Muffle Furnace
X-Ray Powder Diffractometer (XRD)
Fourier Transform Infrared Resonance (FTIR)
Scanning Electron Microscope (SEM)
Energy Dispersive X-RaySpectrometer (EDX)
For Preparation of Cadmium Solution:
Cadmium sulphate ($3CdSO_4.8H_2O$)
Alizarin red s indicator
Sulphuric Acid - H_2SO_4
Sodium Hydroxide–NaOH All the Chemicals used were of analytical grade samples.

2.2. Equipment Used:

For Reduction of Cd(II)
PH Meter
Photo catalytic Reactor
UV Visible Spectrometer

3. Experimental Procedure

3.1. Synthesis of Iron Oxide Nanoparticles:

1mole of Ferric Nitrate solution was prepared by adding 40.408 gram of Ferric nitrate ($Fe(NO_3)_3.9H_2O$) in 100ml of distilled water and was dissolved.100ml of Ethylene Glycol was added in Ferric nitrate solution and was kept for stirring till clear brown solution was obtained. The obtained solution was taken in 500ml round bottom flask and its temperature was maintained at 90°C using reflux condenser for 8 hours with continuous stirring.After 8 hours the solution was centrifuged for 15 min at 11000 rpm at room temp (25^0C) and supernatant liquid was removed from the tube.Particles were centrifuged again by using distilled water and acetone as solvent for 5 min at 4000 rpm at room temperature. For removal of impurities and brownish gel was obtained. Gel (amorphous phase) was taken for drying on the watch-glass and was kept in hot air oven at 80^0C for 10 min. NOTE: No moisture should be present. Sample after heating was grinded in crucible, which resulted in formation of a fine brown powder. The powder was calcinated at 400^0C in muffle furnace for 3 hours. After 3 hours, heater was turned off and sample was left in furnace till temperature of 35^0C was attained.

3.2. Prpreparation of Cadmium (II) stock solution

2.3049 gm of Cadmium sulphate octahydrate ($3CdSO_4$.$8H_2O$) was weighed and was diluted in 1000ml of distilled water in volumetric flask up to the mark to get 1000ppm solution. All the required solutions were prepared with analytical grade reagents and distilled water. Synthetic samples of different concentrations 2,4,6,8 and 10 ppm of Cadmium (II) were prepared from this stock solution. The pH of aqueous solution was adjusted to the desired value by adding 0.05N H_2SO_4 or 0.1N NaOH solution.

3.3. Procedure for Reduction of Cadmium (II)

2, 4, 6, 8 and 10ppm solutions prepared were taken for UV analysis to know the absorbance. And the absorbance was used as reference.100ml of stock solution with predetermined Cadmium (II) concentration and pH was taken in quartz tube.100mg of iron oxide nanoparticles which was synthesized were added into the solution. Cadmium (II) solutions in quartz tubes were placed in photo catalytic reactor. Where the solution was exposed to visible light source. After every 30min. 1ml of sample was collected and the collected samples were centrifuged using microcentrifuge, later 1ml of alizarin red s indicator solution and 0.1 ml of acid were added **.**The solution was taken for U.V analysis to know the absorbance**.**

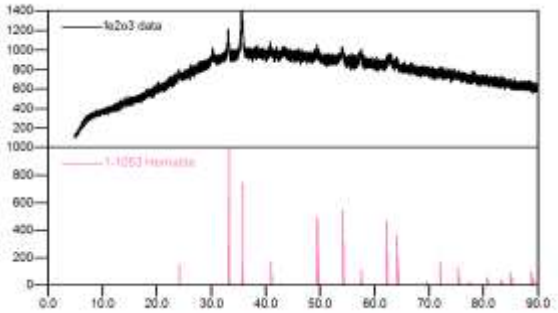
4. Variation of Parameters:

PH maintained for the solutions of different concentrations were 4,5,6,7 and 10. Concentration of cadmium solution varied were 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.

5. Results and Discusions

5.1. Characterisation of Iron Oxide Nanoparticles

X-Ray Powder Diffraction



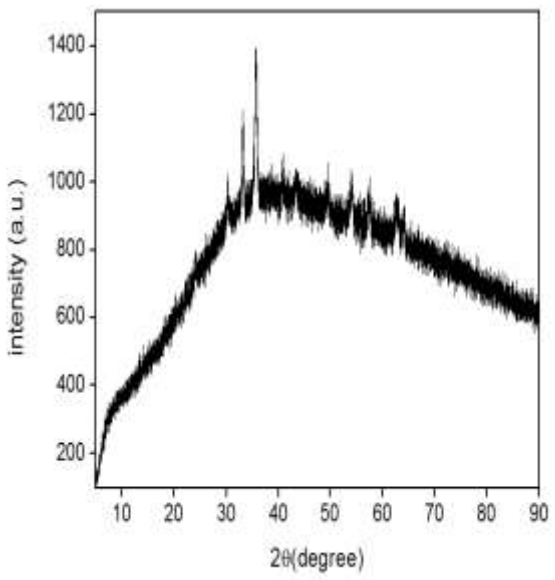


Fig: XRD graph for αFe_2O_3 Nanoparticles.

The obtained iron oxide nanoparticle was identified as α-Fe_2O_3 (Haematite) on comparison with obtained spectra against Joint Committee on Powder Diffraction Standards Database (JCPDS). As temperature increases, the intensity of the diffraction peaks of the samples increases and the peak width at half maximum decreases, indicating an improvement of crystallinity. The analyzed material is finely ground, homogenized, and average bulk composition is determined.[9]

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.
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.**

5.2. Fourier Transform Infrared Resonance

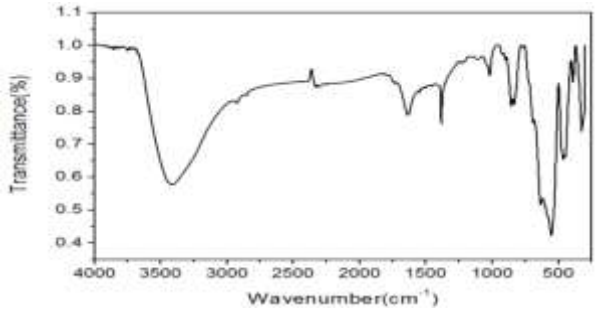
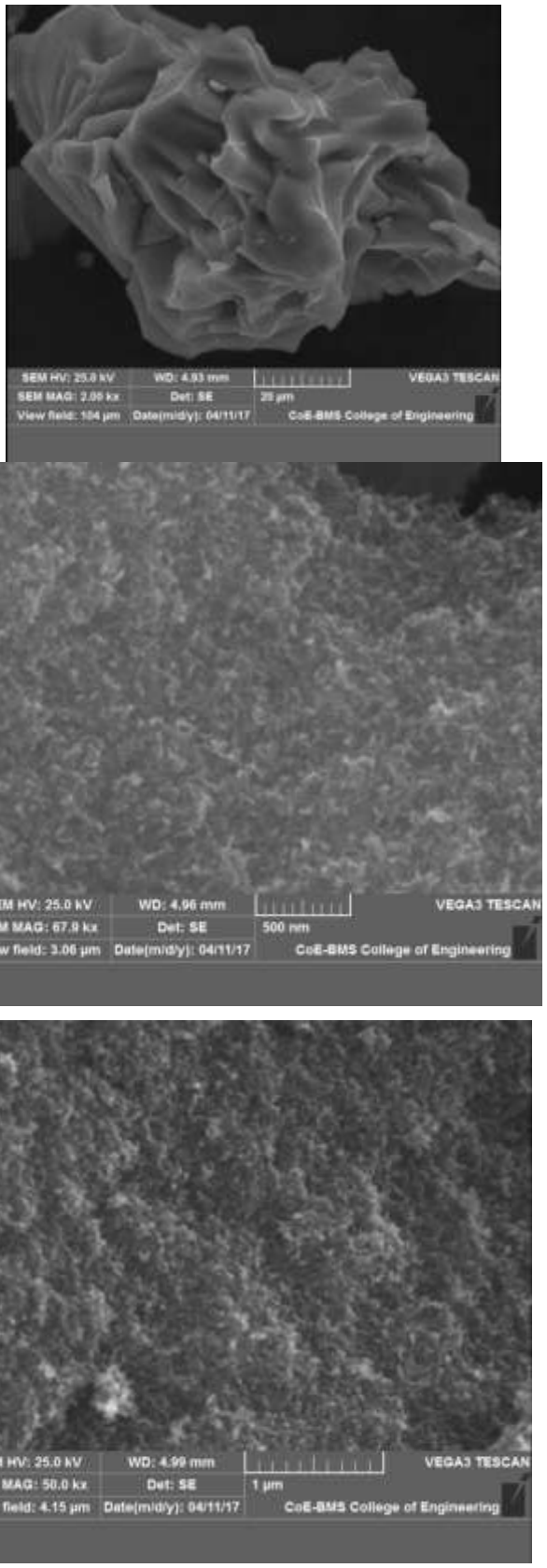


Fig: graph for α-Fe_2O_3 Nanoparticles.

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 are 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.

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

5.3. Sem Analysis



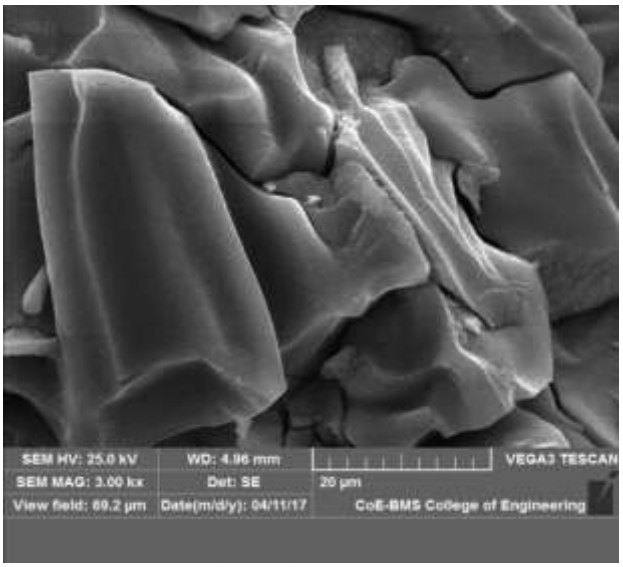


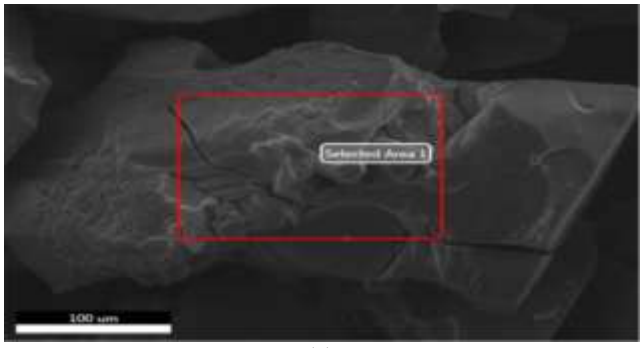
Fig: SEM images for α-Fe_2O_3 Nanoparticles.

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

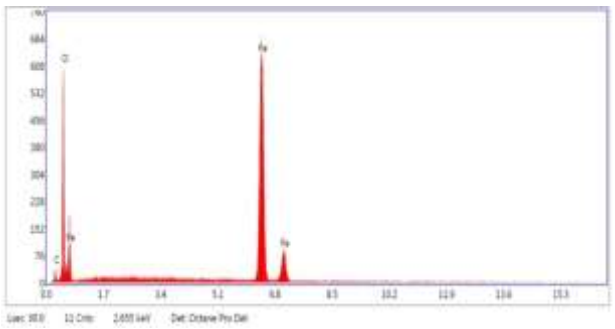
EDX

Energy-dispersiveX-ray spectroscopy (EDS, EDX, EDXS or XEDS),sometimes called energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA), is an analytical technique used for the elemental analysis or chemical characterization of a sample[11]. EDX of the precursor shows only the elements C, O, and Fe are present.

5.4. Selected Area.



(a)



kV:25 , Mag :624, Time(S):30, resolution(eV):123.3

(b)

Fig: (a) EDX Image of IONP; (b) Graph of EDX

6. Results:

Element	Weight %	Atomic%	Net Int.	Error%	Kratio
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

6.1. Reduction of Cd (Ii) to Cd (0) Using Iron Oxide Nanoparticles

The chemistry behind the photo catalytic reduction is that, iron oxide nano particles having Fe^{2+} oxidation state converts to Fe^{3+} oxidation state.[12]

Visible light

$2Fe^{2+} \longrightarrow 2Fe^{3+} + 2e^-$

$2e^- + Cd^{+2} \longrightarrow Cd^{+0}$

During this conversion it donates electron to cadmium heavy metal ions and cadmium ion get reduced to non-toxic form i.e from Cd^{2+} to Cd^{+0} states. The reduction can be identified by UV-vis spectrophotometry. For the photo reduction of cadmium heavy metal photo catalytic reactor is used under visible spectrum. The photo catalytic reactor used was of 125 watts. Experiments are done on various parameters such as time, dosage, concentration and pH and optimum results are found at which maximum removal took place.

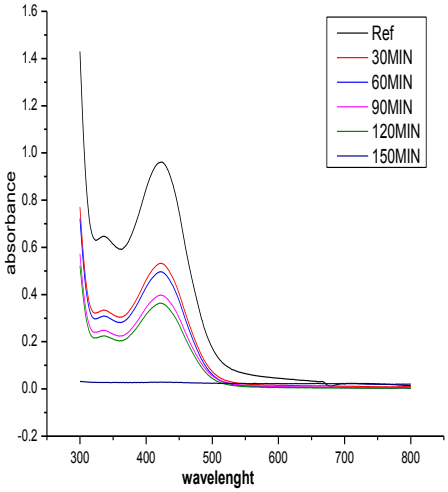
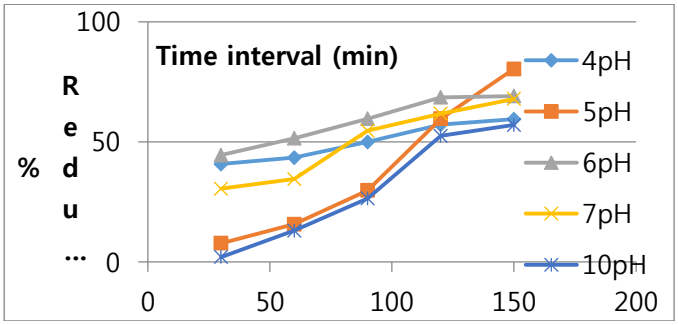
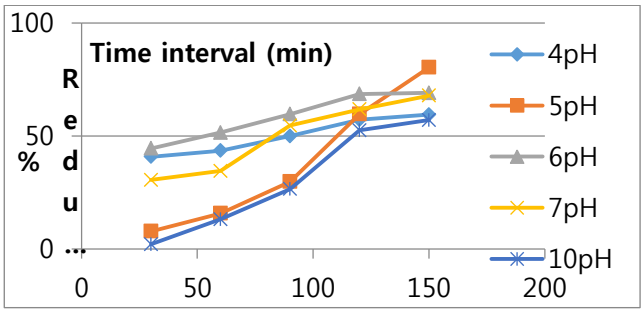


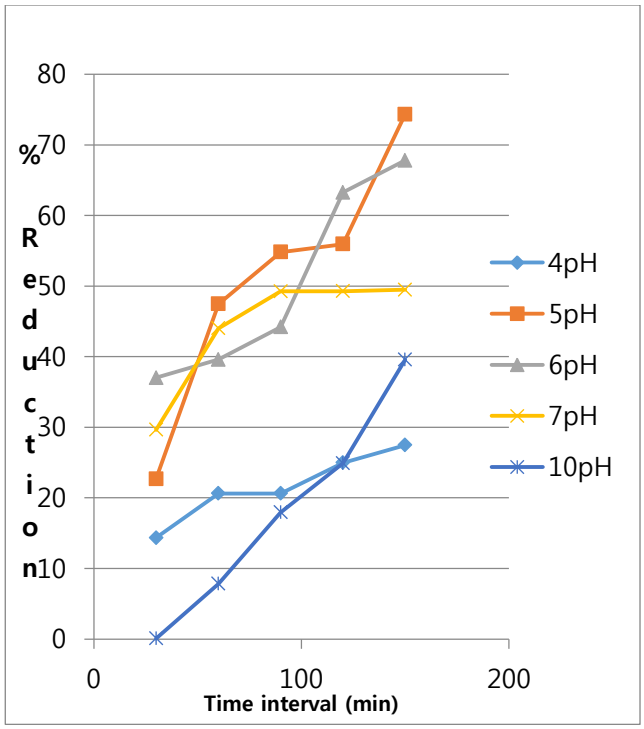
Fig1: UV-Vis absorbance graph (4ppm, 100mg dosage, 5pH)



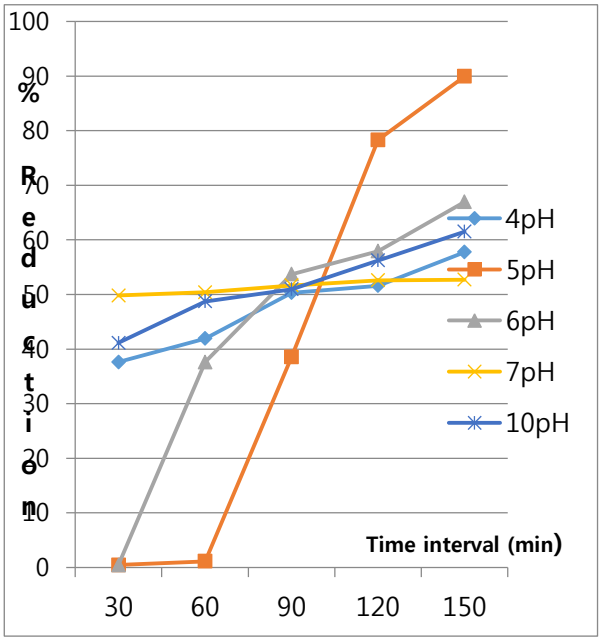
Graph 1: % Reduction vs time interval at dosage 100mg INOP and 2ppm concentration for different pH.



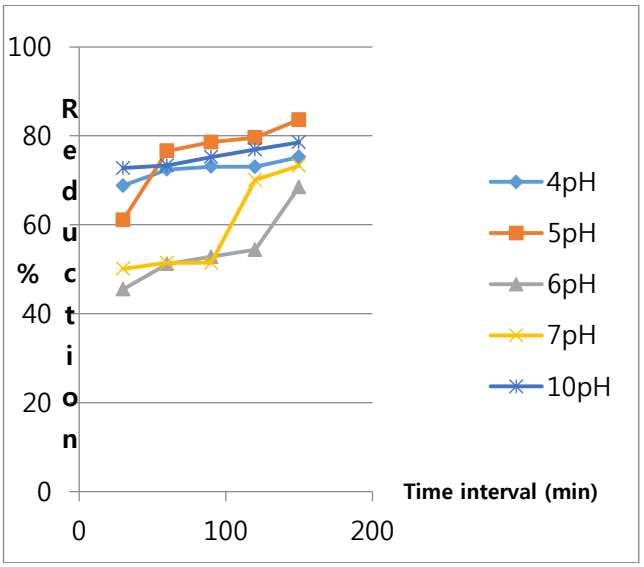
Graph.2: % Reduction vs time interval at dosage 100mg and 4ppm constant at different pH



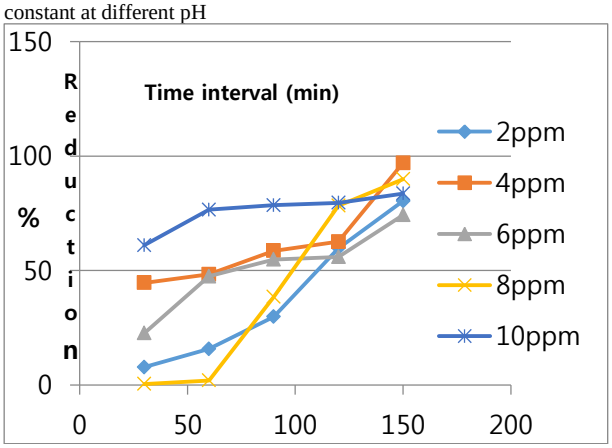
Graph.3: % Reduction vs time interval at dosage 100mg and 6ppm constant at different pH



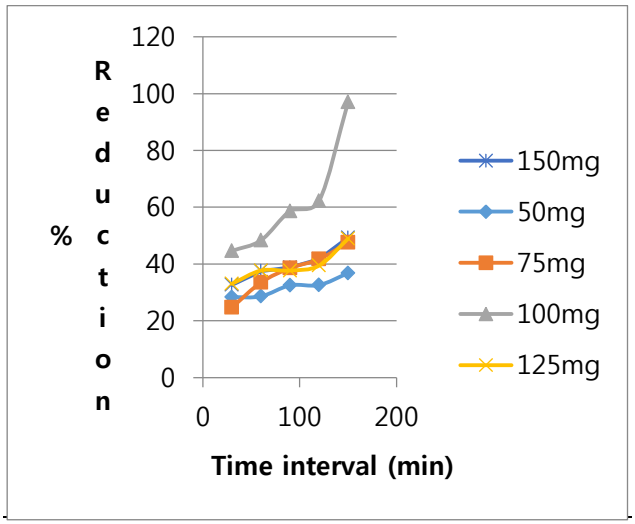
Graph.4: % Reduction vs time interval at dosage 100mg and 8ppm constant at different pH



Graph.5: % Reduction vs time interval at dosage 100mg and 10ppm constant at different pH



Graph.6: % Reduction vs time interval at dosage 100mg and 5pH constant at different concentration (ppm).



Graph.7: % Reduction vs Time interval at 4ppm and 5pH constant at different dosage.

In graph.1, 2, 3, 4 and 5 keeping dosage 100mg and concentration 2ppm, 4ppm, 6pmm, 8pmm and 10ppm constant respectively with variation in pH the highest reduction of 80.39%, 97%, 74.3%, 89.95% and 83.63% were found respectively. Therefore, we can conclude that the maximum reduction was obtained at 5pH. Graph.6 shows that at 5pH and 100mg dosage constant at different concentration maximum reduction of 97% was found at 4ppm.Since, best results were found at 4ppm & 5pH, keeping

them constant, variation in dosage were made and the maximum reduction was obtained at 100mg of dosage.

7. Conclusion

The iron oxide nanoparticles prepared by Sol-Gel method was found to be hematite by XRD. Flowered structured images were taken from SEM and presenenceironoxide and functional groups were confirmed by FTIR. The size and shape was confirmed using SEM. Iron oxide (Fe_2O_3) Nanoparticles were synthesized with 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 were confirmed by EDX. At higher calcination temperature at 400^0C better XRD peaks were obtained ,which confirms the Hematite(α-Fe_2O_3) on comparison with obtained spectra against Joint Committee on Powder Diffraction Standards Database(JCPDS). In this work, Iron Oxide Nanoparticles were used as an effective photo catalyst for the reduction of Cd (II) under UV-vis radiation (125 watts) source. The Nanoparticles with small crystalline size and strong visible-light absorption were appropriate for the photo catalytic reduction of Cd (II). The effect of pH was investigated in reduction. The catalyst showed high reduction in acidic medium that is appropriate for the complete reduction at 5pH. 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 photo absorption, and reduction.According to the results, maximum metal reduction Efficiency (%) for Cd(II) were obtained at: pH 5; Contact time of 150minutes; Fe_2O_3 dosage 100mg; Metal concentration 4ppm.

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