Synthesis and Characterization of Magnetic Nanocomposites using Oxides of Fe & Cu, Chitosan and Onion

Shekhar L. Pandharipande, Aakruti B. Makode

Abstract— **Water pollution has become a global problem with progression of modern industries and has attracted attention of one and all in recent years. Chitosan is being considered as an adsorbent for removal of pollutants from water. This is due to its efficiency compared with activated carbons and other adsorbents. The objective of present work is to synthesize Fe_2O_3/$CuFe_2O_4$/chitosan magnetic nanocomposites. Onion extract is used as a reductant for green synthesis of magnetic nanocomposites. The nanocomposites show ferromagnetic behavior tested by applying magnet to the material synthesized. The effects of onion and chitosan amount on the morphology and particle size of nanocomposites are investigated. The method is proved to be a new, simple, efficient and quick way. Characterisation of samples synthesized indicated that magnetic nanocomposites were formed successfully. The added advantage of these types of composites is in its ease of separation from treated wastewater.**

***Index Terms*—adsorption, chitosan, green synthesis, magnetic nanocomposite.**

I. INTRODUCTION

Water pollution has become a global problem with progression of modern industries and has attracted attention of one and all in recent years. The elementary pollutants include biodegradable waste, dyes, metals, phosphates and nitrates, fluoride, hazardous and toxic chemicals, radioactive pollutants, pharmaceuticals and personal care products. Trace amounts of any of these compounds lead to an enormous pollution problem and consequently, the treatment of wastewater is a subject of paramount importance. Several conventional techniques such as solvent extraction, photocatalytic degradation, chemical coagulation and biodegradation have been developed for removing various pollutants but adsorption has become a widely used technology for the removal of both inorganic and organic material.

In recent years, extensive attention has been paid to the performance of chitosan as an adsorbent for pollutants from water. This is due to its efficiency compared with activated carbons and other adsorbents. However after the process of adsorption is complete, it becomes difficult to separate chitosan-based adsorbents from the aqueous solution using traditional separation methods such as filtration and sedimentation. This is due to adsorbents blocking filters. Furthermore, the adsorbents discarded with the process sludge generate secondary pollution. To overcome the problems related to the ease of separation and regeneration of adsorbents, recent research has been focused on magnetic separation technology. Separation technologies employing magnetic adsorbents are an alternative method for treating wastewater that has received considerable attention in recent years. The main advantage of this technique is that a large amount of wastewater can be purified in a very short period of time using less energy and producing no contaminants.

Herein, the objective of present work is to synthesize Fe_2O_3/$CuFe_2O_4$/chitosan magnetic nanocomposite using onion extract as a reductant via sol-gel auto combustion route. Onion has biological properties such as antibiotic, antioxidant, antidiabetic etc. Being antioxidant in nature it helps to reduce the ions into atoms which then nucleate to form small clusters and to stabilize nanoparticles against aggregation by steric repulsion. The nanocomposite synthesized is analysed using characterization methods.

II. LITERATURE REVIEW

A brief summary of the research and review papers which were referred for the present work is given below:

a. Paper titled "Synthesis and characterization of Fe_3O_4 and ZnO nanocomposites by the sol– gel method[1] ", reports the synthesis of magnetite (Fe_3O_4) nanoparticles from ferric nitrate ($Fe(NO_3)_3.\ 9H_2O$) and ethylene glycol ($C_2H_6O_2$) in inert atmosphere using the sol–gel method. In the next stage, composite nanopowders of Fe_3O_4–ZnO were obtained from zinc acetate and diethanolamine via the sol–gel method followed by drying of precursor and then annealing in vaccum furnace at different temperatures. The formation of Fe_3O_4–ZnO nanocomposites was further confirmed by XRD.

b**.** The special feature of the paper "$NiTiO_3$/$NiFe_2O_4$ nanocomposites: Simple sol–gel auto-combustion synthesis and characterization by utilizing onion extract as a novel fuel and green capping agent[2] ", is to utilize onion extract as a novel fuel and green caping agent in the synthesis of $NiTiO_3$/$NiFe_2O_4$ nanocomposites. In their work a sol of $NiFe_2O_4$ was obtained first, from metal nitrates and onion extract as reductant. Then a sol of titanat was prepared by mixing of tetra-n-butyl orthotitanate, diethanolamin and ethanol and was added to the $NiFe_2O_4$ sol. The significant effect of molar ratio of Ti to Ni on morphology, magnetic properties, purity and phase of nanocomposites was studied.

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***Shekhar L. Pandharipande**, Department of Chemical Engineering, Associate Professor, Laxminarayan Institute of Technology, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur, India, +91-9823360705*

***Aakruti B. Makode,** Department of Chemical Engineering, Student, Laxminarayan Institute of Technology, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur, India, +91-7709149170*

c. Paper titled "Application of magnetic chitosan composites for the removal of toxic metal and dyes from aqueous solutions[3] ", reports that magnetic chitosan composites (MCCs) are a novel material that exhibits good sorption behavior toward various toxic pollutants in aqueous solution. These magnetic composites have a fast adsorption rate and high adsorption efficiency, efficient to remove various pollutants and they are easy to recover and reuse. The main objective of this review is to provide up-to-date information about the most important features of MCCs and to show their advantages as adsorbents in the treatment of polluted aqueous solutions.

d**.** Paper titled as "Green synthesis of magnetic chitosan nanocomposites by a new sol-gel auto-combustion method[4] ", reports that the $Fe_2O_3/CuFe_2O_4$/chitosan nanocomposites have been successfully synthesized via a new sol-gel auto-combustion route utilizing onion as a green reductant for the first time and chitosan was used to functionalize and modify the nanostructures and also to improve surface properties. The nanocomposites were also characterized by several techniques including SEM, TEM, XRD, IR and VSM.

III. PRESENT WORK

The objective of present work is to synthesize the Iron oxide- Copper ferrite - Chitosan magnetic nanocomposites using onion extract as a green reductant employing sol gel process. The claim is to be validated by following appropriate characterization methods.

The work is divided into three parts:-

1. Synthesis of iron oxide-copper ferrite mixture using onion juice as green reductant by employing sol gel process.
2. Synthesis of nanocomposites using chitosan.
3. Characterization of magnetic nanocomposites synthesized.

A. METHODOLOGY

The methodology adopted in present work is depicted in flowchart Fig. 1 whereas pictorial representation is shown in Fig. 2 :

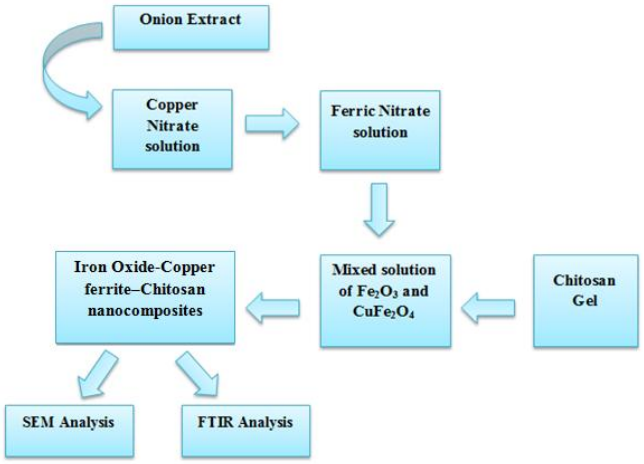


Fig. 1: Methodology

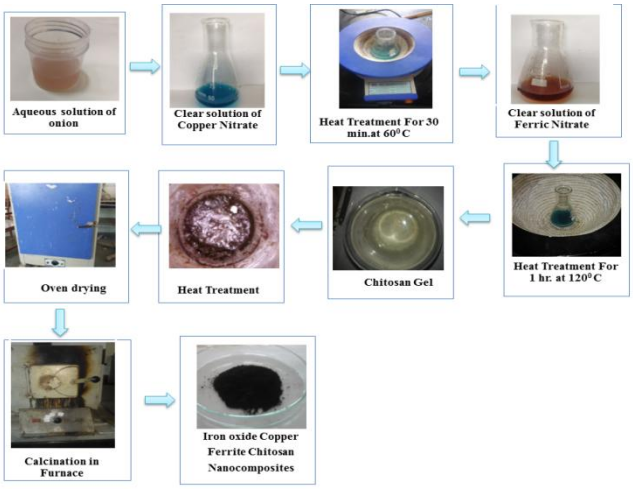


Fig. 2: Pictorial representation of the Methodology

B. MECHANISM

It is suggested that the following reactions occur during the calcination process. The $Fe(NO_3)_3$ and $Cu(NO_3)_2$ salts are decomposed. Reaction of the Fe_2O_3 with the CuO is caused due to formation of $CuFe_2O_4$. The Fe_2O_3, $CuFe_2O_4$ and chitosan are combined together to form the $Fe_2O_3/CuFe_2O_4$/chitosan nanocomposites[8].

C. PROCEDURE

Part 1: Synthesis of $Fe_2O_3/CuFe_2O_4$ Mixture.

1. Known amount of copper nitrate crystals were weighed and taken into beaker. Distilled water was added till the clear solution of copper nitrate was formed.
2. The onion juice was extracted and its aqueous solution was prepared.
3. The known amount of aqueous solution of onion was added to copper nitrate solution, dropwise, under constant stirring at room temperature.
4. This solution was heated by stirring at 60^0C for 30 minutes.
5. Known amount of ferric nitrate crystals were added with distilled water to form clear solution of ferric nitrate.
6. The ferric nitrate solution was added to the solution prepared and heated to 120^0C by stirring for 1 hour. The viscous gel was formed.

Part 2: Synthesis Of $Fe_2O_3/CuFe_2O_4$ /Chitosan Magnetic Nanocomposites.

1. 0.5 gm of chitosan flakes were taken intsssssso beaker. To this 40 ml. of water and 2 ml. of acetic acid was added. The entire mixture is heated till the highly viscous chitosan gel was formed.
2. The chitosan gel was added to the gel prepared in part 1. The entire mixture was heated so as to vaporize water.
3. The product obtained was oven dried at 100^0C followed by calcination in furnace at 600^0C.

D. OBSERVATION TABLE

Sample No.	Ferric Nitrate Solution		Copper Nitrate solution		Onion juice (ml)	Chitosan (gm)	Yield (gm)
	Amount of $(FeNO_3)_3.9H_2O$ (gm)	Amount of water (ml)	Amount of $Cu(NO_3)_2$ (gm)	Amount of water (ml)			
FC-1	6.88	5.1	3.38	4.1	1	0.5	1.04
FC-2	16.86	18.8	7.83	13.	5	1	4.38
FC-3	16.93	19.1	7.93	13.4	-	1	5.4
FC-4	16.93	19.1	7.93	13.4	13.5	-	-
FC-5	16.97	19.1	7.93	13.4	34	0.1245	-

Table I. Process parameters for synthesis of magnetic nanocomposites.

The details of process parameters of magnetic nanocomposites synthesized in present work are given in Table I.

E. CHARACTERIZATION

The characterization of the prepared samples FC-1 to FC-5 was done by SEM & FTIR analysis.

1. SEM analysis

The SEM analysis is to study the morphology and crystallinity of obtained products. SEM characterization indicated the nanocomposites were formed successfully.

The nanocrystalline surface morphology can be observed from SEM images of sample FC-1 and FC-2 as shown in Fig. 3.a and 3.b. Basically it is non-homogeneous particulate matter having particle size ranging approximately between 600 nm – 3800 nm and 400 nm - 3600 nm respectively. From Fig. 3.c it can be inferred that the particles formed have been agglomerated and have non-homogeneous surface with irregular patterns. The agglomeration of particles and irregularity in particle size can be because of presence of organic matter i.e. chitosan. From Fig. 3.d it can be seen that there is formation of bulk structure. This may be due to use of high proportion of onion juice. Fig. 3.e shows formation of the irregular prisms and layered hexagonal plates with varying faces whose size ranges between hundredths of nanometers to few microns.

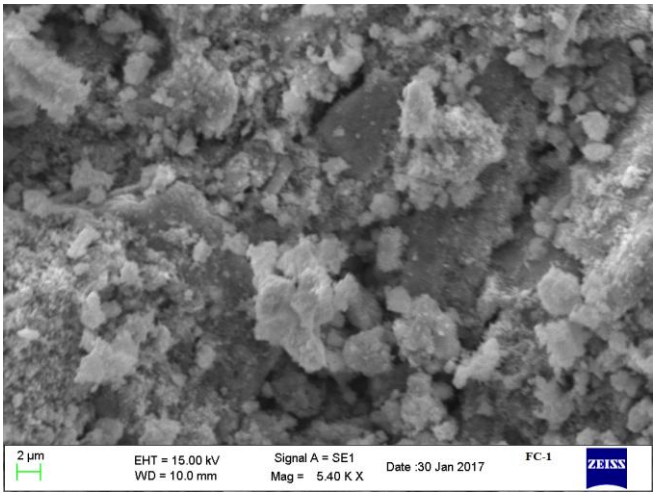


Fig. 3.a

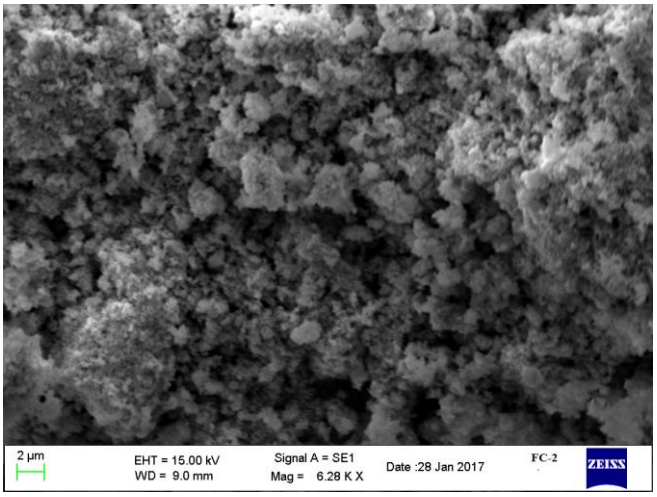


Fig. 3.b

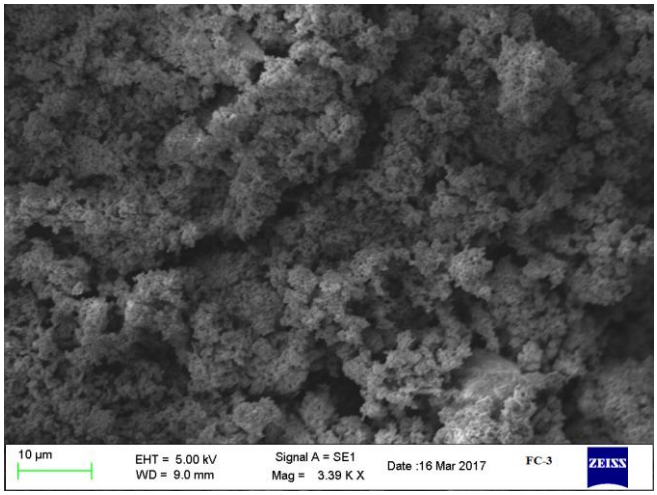


Fig. 3.c

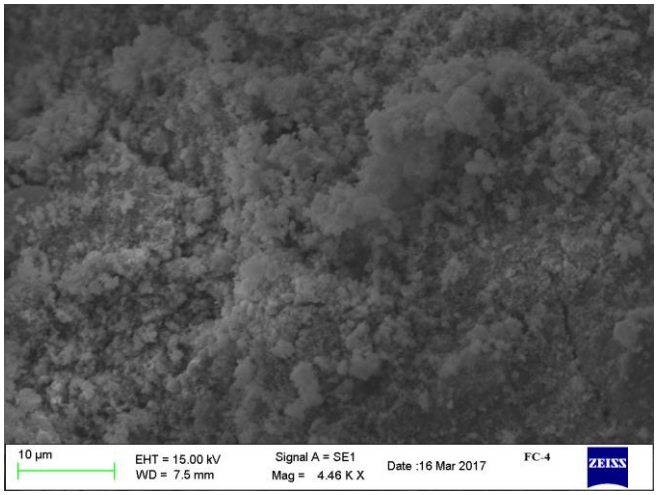


Fig. 3.d

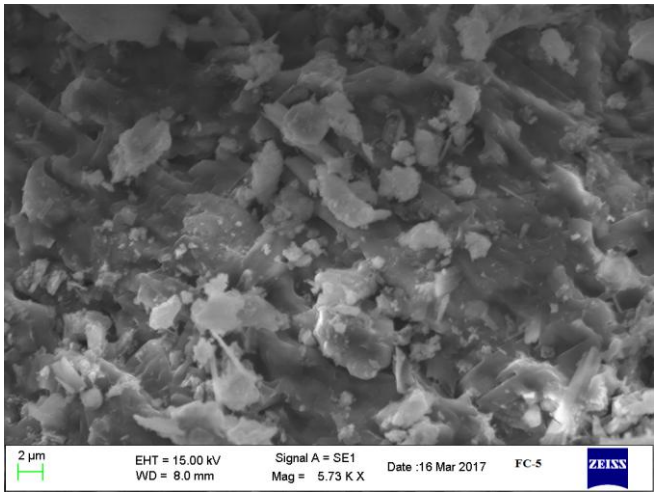
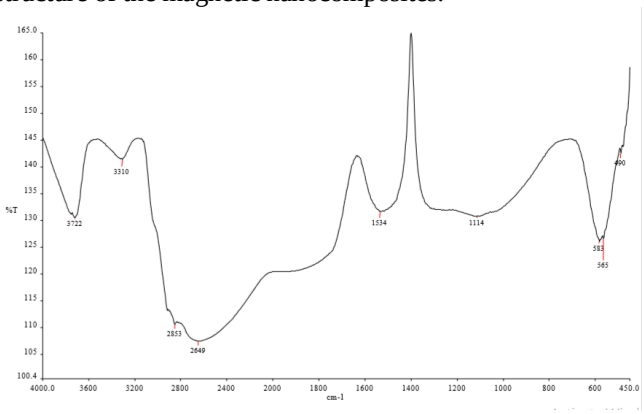


Fig. 3.e

Fig.3: SEM images of the nanocomposites synthesized: (a) FC-1 (b) FC-2 (c) FC-3 (d) FC-4 (e) FC-5

2. FTIR Analysis

FT-IR spectroscopy is one of the most important and widely used analytical methods for obtaining information about the presence of certain functional groups in the structure of the magnetic nanocomposites.



Fig, 4: FTIR spectra for sample FC-2

Fig.4 shows FT-IR spectra for sample FC-2 of $Fe_2O_3/CuFe_2O_4$/chitosan magnetic nanocomposites. The interpretation of peaks obtained is carried out by comparison with that of nanocomposite, onion juice and chitosan reported in literature and the summary is given in Table II.

In FTIR spectrum of sample FC-2 the absorption band at 3722 cm^{-1} is attributed to O-H stretching. The band corresponding to Fe-O stretching vibrations is positioned at 583 cm^{-1} As value obtained from literature[6] for FTIR spectra of copper ferrite for Fe-O stretching vibration bond is 578.12, this confirms the presence of copper ferrite in product synthesized. Most studies have shown the chitosan exhibits the following peaks: ~3436 cm^{-1} due to N-H stretching vibrations, ~1550 cm^{-1} due to NH_2 bending vibrations and ~1382, 1083, 1023 cm^{-1} due to C-O stretching vibrations[4]. In FTIR spectrum of sample FC-2, we have obtained the peaks at 3310 cm^{-1}, 1534 cm^{-1} and 1114 cm^{-1} thus this confirms the presence of chitosan in product FC-2.

Also literature values for onion exhibits the following peaks[5] : 2900-3800 cm^{-1} due to C-H stretching vibrations, 1600-1500 cm^{-1} due to carboxylic groups , 1150-950 cm^{-1} due to $-PO_4^{3-}$ group and 650-480 cm^{-1} due to N-containing bioligands. In FTIR spectrum of sample FC-2, we have obtained the peaks at 2853 cm^{-1}, 1534 cm^{-1} and 1114 cm^{-1} and 490 cm^{-1}, thus this confirms the presence of onion in product FC-2. The peak at 3722 cm^{-1} relates to O-H stretching vibrations, 2649 cm^{-1} relates to presence of chelate compounds, 1114 cm^{-1} relates to C-O group and 565 cm^{-1} relates to C-C bond based on literature values[4],[7]. These functional groups and bonds may be because of interactions between ferrites and polysaccharide type biopolymers.

Overall, the FT-IR spectrum provides supportive evidence that the surface of $Fe_2O_3/CuFe_2O_4$ nanostructures are successfully coated with chitosan chains.

Sr. no	Functional groups	Wave number peaks in sample FC-2 (cm^{-1})	Wave number identified from literature[4] (cm^{-1})	Wave number in FTIR of onion[5] (cm^{-1})	Wave number in FTIR of chitosan[4] (cm^{-1})	Wave number in FTIR of Copper ferrite[6] (cm^{-1})
1.	O-H stretching	3722	3439			
2.	N-H stretching	3310			~3436	
3.	C-H stretching	2853		2900-2800	1411	
4.	Chelate compounds, alcohols and phenols	2649				
5.	Carboxylic groups	1534		1600-1500		
	NH_2 bending				~1550	
6.	C-O group	1114	1409,1102,1024		~1382,1083,1023	
	$-PO_4^{3-}$			1150-950		
7.	Stretching vibration of tetrahedral sites due to Fe – O bond	583	615			578.12
8.	C-C	565				
9.	N- containing bioligands	490		650-480		

Table II: Interpretation of FTIR analysis.

IV. RESULTS AND DISCUSSIONS

1. The iron oxide-copper ferrite mixture was prepared successfully.
2. Fig. 5 shows particles of iron oxide-copper ferrite-chitosan nanocomposites attracted by a bar magnet. It shows that magnetically active iron oxide-copper ferrite -chitosan nanocomposites were synthesized successfully.
3. The characterization of synthesized magnetic nanocomposites was also studied successfully.

Fig. 5: Particles of iron oxide-copper ferrite-chitosan nanocomposites attracted by a bar magnet

V. CONCLUSION

This study reports a two-steps route for obtaining magnetic nanocomposites consisting of Fe_2O_3, $CuFe_2O_4$ and chitosan by sol-gel auto-combustion route. The nanocomposites show ferromagnetic behavior tested by applying magnet to the material synthesized. . The effects of onion and chitosan amount on the morphology and particle size of nanocomposites are investigated. The method is proved to be a new, simple, efficient and quick way. Characterisation of samples synthesized indicated that magnetic nanocomposites were formed successfully. The added advantage of these types of composites is in its ease of separation from treated wastewater.

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AUTHORSs

Shekhar L. Pandharipande is working as associate professor in Chemical Engineering department of Laxminarayan Institute of Technology, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur. He did his master in 1985 & joined LIT as a Lecturer. He has coauthored three books titled, "Process Calculations", "Principles of Distillation" & "Artificial Neural Network". He has two copyrights "elite-ANN" & "elite-GA" to his credit as coworker & has more than 60 papers published in journals of repute.

Aakruti B. Makode has completed B.Tech in Chemical Engineering from Laxminarayan Institute of Technology, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur (2017).