Synthesis and Characterization of PAN/GO/Iron Oxide Composite Nanofibers Membrane for Adsorption of Congo red dye from aqueous solution

A dissertation submitted in partial fulfilment

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Under Academic Autonomy

NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA

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GUIDE CERTIFICATE

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This is to certify that the dissertation entitled "Synthesis and Characterization of PAN/GO/Iron Oxide Composite Nanofibers for Adsorption of Congo Red dye from aqueous solution" by Smruti Prangya Behera (Roll No.: 413CY2005) to the department of chemistry, National Institute of Technology, Rourkela for the degree of Master of Science in Chemistry is based on the result obtained in the bonafide project work carried out by her under my Guidance and supervision.

I further certify that to the best of my knowledge Smruti Prangya Behera bears a good moral character.

Dr. G. Hota

N.I.T, Rourkela ***Date:5/05/2015***

DECLARATION

I Smruti Prangya Behera hereby declare that this project report entitled "Synthesis And Characterization of PAN/GO/Iron Oxide Nano composite Fiber For adsorption of Congo Red dye from aqueous solution " is the original work carried out by us under supervision of Dr. G. Hota, Department of chemistry, National Institute of Technology Rourkela (NIT), Rourkela and the present work or any other part thereof has not been presented to any other University or Institution for the award of any other degree regarding to our belief.

Smruti Prangya Behera

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Smruti Prangya Behera

ABSTRACT

In the present study, we have synthesized PAN/GO/ϒ-Fe_2O_3 composite nanofibers membrane by electrospinning method. Prior to this, first we have synthesized graphene oxide (GO) by advanced Hummer's method and Maghemite (ϒ-Fe_2O_3) nanoparticle by sol gel method. These nanoparticles were impregnated with polyacrylonitrile (PAN) solution in DMF solvent and then electrospinning these composite solutions to obtain of PAN/GO/ϒ-Fe_2O_3 composite nanofibers. The formation, surface morphology and crystalline phase of PAN/GO/ϒ-Fe2O3 composite nanofibers were characterized by FTIR (Fourier Transform Infrared) spectroscopy, FE-SEM (Field emission Scanning Electron Microscope) and XRD (X-Ray Diffraction) analytical techniques. The synthesized PAN/GO/γ-Fe2O3 composite nanofibers have been used as adsorbent materials for the removal of Congo red dyes from the aqueous solution. The batch experiments were carried out for the adsorption studies of Congo Red dyes. The results shows that PAN/GO/ϒ-Fe_2O_3 fibers are good adsorbents for the removal of Congo red (CR) dyes from aqueous solution.

Key words: Composite nanofibers, electrospinning, Adsorption, Congo red dye

CHAPTER 1

INRODUCTION

1.1 Nanoscience & Nanotechnology

This is a field of applied science, focused on the design, synthesis, characterization and application of materials and devices on the nanoscale. This is a sub classification of technology in colloidal science, physics, chemistry and other scientific fields and involves the study of phenomena and manipulation of material at the nanoscale, in essence an extension of existing sciences into the nanoscale [1].

1.2 Nanomaterials

"The design, characterization, production, and application of structures, devices, and systems by controlled manipulation size and shape at nanometer scale (atomic, molecular, and macromolecular scale) that produces structures, devices and systems with at least one novel/superior characteristic or property" is the accepted definition of Nanomaterials", Nanomaterials are materials, where the sizes of the individual's building blocks are less than 100nm, at least in one dimension.

1.4 Electrospinning technique

Electrospinning is a technique to produce nanofibers more efficiently.In electrospinning, electricity spin fibers by extracting the polymer from the solvent and stretching it, all in one continuous electricfield.This is an electrostatic fiber fabrication technique has evinced more interest and attention in recent years due to its versatility and potential for applications in diverse fields.The notable applications include in tissue engineering, biosensors, filtration, wound dressings, drug delivery, and enzyme immobilization [2].

1.5 Objective Overview

- To prepare Graphene oxide by modified Hummer's method.
- To prepare iron oxide nanoparticles by sol gel method followed by calcination.
- To prepare Graphene oxide doped PAN/Iron oxide nanocomposite fibers by electrospinning technique.
- Characterization of Graphene oxide doped PAN/Iron oxide nanocomposite fibers by FTIR, XRD and FE-SEM analytical techniques

CHAPTER 2

EXPERIMENTAL SECTION

Materials and methods

2.1 Materials

Graphite powder, DMF, ammoniacal solution, Hydrogen peroxide and Iron chloride were procured form Merck Specialties Pvt. Ltd.; PAN from Sigma-Aldrich; Ferric Nitrate and Sodium Nitrate were from Nice Chemical Ltd. All chemicals were used without further purifications. Double distilled water was used in throughout the experiment.

2.2 Synthesis of graphene oxide by modified Hummer's method:

For Graphene Oxide the required chemicals were Graphite powder (2g, 500 mesh), Sodium Nitrate (1g), conc.H_2SO_4 (7ml, 30%), HCl (55ml). 2gm graphite and 1gm Sodium Nitrate were mixed 50 ml concentrated H_2SO_4 in a 250ml flask at 0^0C .The temperature was kept at 5^0C and the mixture was stirred for 2 hrs. Then 7.3 gm of $KMnO_4$ was added in small portions to prevent temperature rise in excess of 20^0C. Then temperature of the reaction mixture was raised to (35-37)^{0}C and the mixture was stirred for 30 minutes. After completion of the reaction, 90 ml of deionized water was added gradually into the solution. The suspension was reacted further by adding a mixture of 7ml H_2O_2 i.e. of 30% and 55ml of water was added. The Graphite Oxide was separated from the reaction mixture by filtration .The yellow brown graphite oxide powders were washed three times with warm diluted HCl of 150 ml (30%) and then dried under reduced pressure for 24 hrs. to obtain the Graphene Oxide powder.

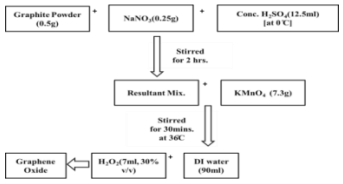

Fig 2.1 Flowchart of preparation of graphene oxide

2.3 Synthesis of Maghemite Nanoparticles:

For Maghemite Nanoparticles the required chemicals were $FeCl_2.4H_2O$ (1g), $Fe(NO_3)_3.9H_2O$ (1.5g),Ammonium Hydroxide 20 ml (10%) . Both, the $FeCl_2.4H_2O$ (1g) and $Fe(NO_3)_3.9H_2O$

(1.5g) are mixed together with 50ml water and 37ml water respectively in the ratio of 2:3 .Then the solution was stirred for 2 hrs. at temperature 70^0C . A black color precipitate was formed which was then subjected for wash for several times to eliminate the residual chloride. The product was kept for cooling in a desiccator. The magnetite (Fe_3O_4) nanoparticle was thus formed in blackish red color which upon calcination for 5 hrs. at 250^0C yielded Maghemite nanoparticle in reddish brown color.

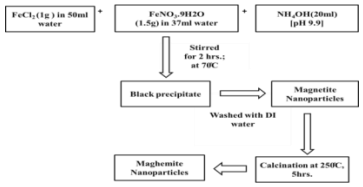

Fig 2.2 Flowchart of Maghemite Nanoparticle synthesis

2.4 Synthesis of PAN/GO/Iron Oxide composite nanofiber by Electrospinning method

The electrospinning setup used in this study consisted of a syringe pump, 2 ml plastic syringe, metallic needle, grounded metal electrode, aluminium sheet, a high voltage power supplier. PAN solution (8 wt %) was prepared by dissolving PAN polymer powder in DMF, as solvent and mechanical stirring was applied for 12 h in order to obtain a homogeneous clear PAN solution. Then 1 wt % graphene oxide and 25 wt % γ-Fe_2O_3 was added to the homogeneous PAN solution by maintaining the polymer to nanoparticle ratio at 4:1. Then again mechanical stirring was applied for 12 h to prepare PAN/GO/Iron oxide homogenous electrospinning solution. Then the resulting solution was loaded into a 2 mL plastic syringe fitted with a metallic needle. Then, the syringe was fixed on the syringe pump and the electrospinning solution was pumped with a flow rate of 1 mL/h. The distance between the needle tip and grounded metal collector was kept constant at 10 cm. A high voltage of 12 kV was applied to the polymer solution by using high voltage power supply.

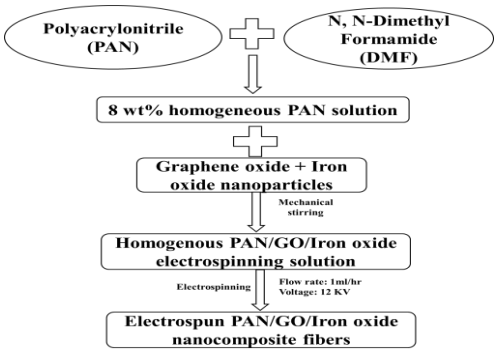

Fig 2.3 flow chart for synthesis of PAN/GO/Iron oxide composite nanofiber

CHAPTER-3
RESULTS AND DISCUSSION

3.1 FTIR ANALYSIS

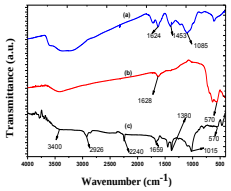

Figure 3.1 FTIR spectra of (a) grapheme oxide, (b) iron oxide nanoparticles, and (c) GO doped PAN/iron oxide nanocomposite fibers

The FTIR spectra of GO, iron oxide and GO doped PAN/Iron oxide nanocomposite were taken in spectral range of 4000-400 cm^{-1} and the spectra are presented in figure 4.1. Figure 4.1 (a) is the FTIR spectra of graphene oxide. The broad peak at around 3050-3600 cm^{-1} is due to O-H stretching vibration, The peaks at 1624, 1453 and 1085 $cm^{-1}$are due to the symmetrical stretching vibration of carbonyl group (-C=O), bending vibration of methylene ($-CH_2-$) group and stretching vibration of C-O group, respectively. Figure 4.1 (b) is the FTIR spectra of iron oxide nanoparticles, where peak at around 570 cm^{-1} represents the stretching vibration of Fe-O groups. Figure 4.1 (c) represents the FTIR spectra of GO doped PAN/iron oxide nanocomposite fibers. From the figure, the peak at around 3400, 1659, and 1015 cm^{-1} are due to the stretching vibration of O-H group, carbonyl group (-C=O), and stretching vibration of C-O group, respectively indicating the presence of graphene oxide. The peak at around 2926 and 2240 cm^{-1} are due to the unsymmetrical stretching vibration of methylene ($-CH_2-$) group and symmetrical stretching vibration of carbonyl group (-CN) group, respectively because of the PAN polymer. Peak at around 570 cm^{-1} represents the stretching vibration of Fe-O groups indicating the presence of iron oxide in the nanocomposite fibers [3].

3.2 X-RAY DIFFRACTION ANALYSIS

X-ray diffraction (XRD) patterns were performed on a Rigaku D/max-2500 diffracto meter with Cu Kα radiation (λ = 1.5418 Å) .The XRD peaks were collected from 2θ = 100 to 800 .The figure 4.1 shows the XRD patterns of (a) GO (b) ϒ-Fe2O3 (c) PAN/GO/G-Fe2O3 .The XRD patterns of maghemite particles (b) obtained at 2500 C for 5 h. The obtained peak s are well match with standard JCPDS File No- 25-1402 according to the match programme. The average crystallite size of the ϒ-Fe2O3 peak is 10.6nm.The major peak for GO (a) is obtained at 100 due to the oxygen functional group of GO as well as water molecules held in the interlayer galleries.

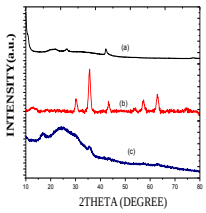

Figure 3.2 XRD pattern of (a) grapheme oxide, (b) iron oxide nanoparticles, and (c) GO doped PAN/iron oxide nanocomposite fibers [4].

3.3 FE-SEM ANALYSIS

In order to study the surface morphology, FE-SEM analysis have been performed. The FE-SEM images of iron oxide nanoparticles along with the EDAX spectrum is shown in figure 4.3. From the figure, it can be observed that the iron oxide nanoparticles are highly agglomerated and the diameters of the nanoparticles are found to in the range of 30-50 nm. In the EDAX spectrum (figure 4.3 (c)), the presence of Fe, O confirms the formation of iron oxide nanoparticles.

Similarly the FE-SEM images of GO doped PAN/iron oxide nanocomposite fibers along with the EDAX spectrum is shown in figure 4.4, which suggests the formation of ultrafine continuous smooth fibers with length up to several micrometers. There are formation of the some bead like structure as shown in figure 4.4 (c), which may be due to the incorporation of GO and iron oxide in the nanocomposite fibers. The presence of C, O, Fe in the EDAX spectrum (figure 4.4(c)) also confirms the incorporation of GO and iron oxide in the nanocomposite fibers [5].

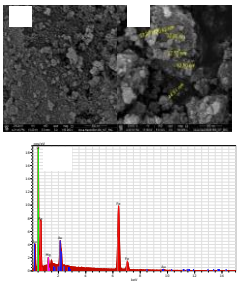

Figure 3.3 (a), (b) FE-SEM images and (c) EDAX spectrum of iron oxide nanoparticle

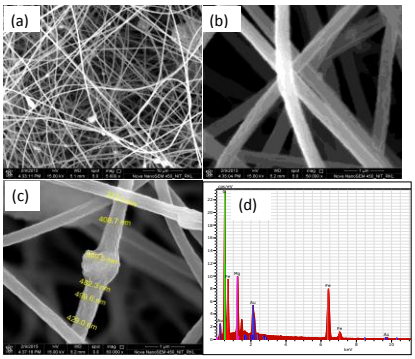

Figure 3.4 (a), (b), (c) FE-SEM images and (d) EDAX spectrum of GO doped PAN/iron oxide nanocomposite fibers

CONCLUSIONS & FUTURE WORKS

CONCLUSIONS

Graphene oxide has been synthesized successfully by modified Hummer's method, iron oxide (γ-$Fe_2O_{3)}$ by sol gel technique and (PAN/GO/γ-Fe_2O_3) composite nanofibers have been synthesized successfully by electrospinning technique, which was confirmed by IR spectroscopy & FE-SEM. Adsorption study for Congo red dyes from aqueous solution was carried out by using electrospun PAN membrane and its composite nanofibers using UV-visible spectroscopy. The effect of time on the adsorption of Congo red dye on the composite nanofibers has been studied. From the experimental results it can be concluded that the synthesized PAN/GO/γ-Fe_2O_3 composite nanofibers membrane has better affinity for Congo Red dye. Therefore, this novel composite PAN nanofibers membrane can be used for the removal of Congo red in different industries and for the environmental application and other aspects.

FUTURE WORKS

- The TEM and XPS characterization of the composite nanofibers need to be carried out.
- Synthesis of reduced GO (rGO) doped PAN/Iron oxide and PAN/Alumina composite nanofibers will be studied.
- Adsorptive removal of different organic pollutants from aqueous stream need to be studied by using the prepared adsorbents.

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