Electrospun PAN nanofibers membrane: Functionalization and Environmental Applications

A Dissertation

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CERTIFICATE

This is to certify that the thesis entitled "**Electrospun PAN nanofibers membrane: Functionalization and Environmental Applications**" being submitted by Shabna Patel (Roll No. – 410CY2023) and Madhusmita Tripathy (Roll No. – 410CY2039) for the partial fulfillment of the requirements for the award of M.Sc. degree in Chemistry at the National Institute of Technology, Rourkela, is an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University or Institute for the award of a degree or diploma.

Date: Signature of the guide:

Place: Dr.Garudadhwaj Hota

DECLARATION

We, Shabna Patel and Madhusmita Tripathy hereby declare that this project report entitled "**Electrospun PAN nanofibers membrane: Functionalization and Environmental Applications**" is the original work carried out by us under supervision of Dr. G. Hota, Department of chemistry, National Institute of Technology Rourkela (NITR), 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.

1st May, 2012 **Shabna Patel.**

Madhusmita Tripathy.

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ABSTRACT

The Polyacrylonitrile (PAN) nanofibers membrane has been synthesized by Electrospinning technique. The functionalization of PAN nanofibers membrane has been done using Ethylenediamine (EDA) and Sodium bicarbonate ($NaHCO_3$). Then the functionalized PAN/ EDA membrane has been used for the removal of Cr (VI) and PAN/ $NaHCO_3$ membrane has been used for the removal of Malachite Green dye from the aqueous solution. The functionalized Electrospun PAN nanofibers were characterized by FTIR, CHNS and SEM-EDAX techniques. The adsorption of Cr (VI) and Malachite green (dye) by the functionalized Electrospun PAN membrane was studied by UV Visible spectroscopy. The effect of contact time, pH and conc. on the adsorption of Cr (VI) and Malachite Green on the functionalized Electrospun PAN nanofibers surface has been studied. The adsorption isotherm and kinetics study was also done for the adsorption of Malachite green dye by functionalized PAN/ $NaHCO_3$ nanofiber membrane. The adsorption of Malachite Green onto functionalized Electrospun PAN membrane fitted well with the Langmuir isotherm equation and follows Pseudo Second Order Kinetics.

1. INTRODUCTION

Any materials having dimensions in the range of 1 to 100 nm are called nanomaterials. They may be zero dimentions (0D), one (1D) or two (2D) dimensional materials. They have relatively high surface area and exhibit quantum size effect. These factors can change or enhance their properties such as reactivity, strength and electrical characteristics. [1, 2]. Now-a-days, among various type of morphology of materials, 1D nano-scaled materials, such as nanofibers have been widely used in almost all areas of Science, Engineering and Technology. Nanofibers can be identified as fibers having diameter between tens and hundreds of nanometers. This nanoscale diameter of fibers can give an enormous surface area per unit volume, high porosity, high gas permeability and small interfibrous pore size. These outstanding properties make the nanofibers to be best candidates for many important applications [3]. These include: adsorption of heavy metal ions and dyes [4,5], filter media [6], composite materials [7], biomedical applications (tissue engineering, scaffolds, bandages, wound healing and drug release systems) [8].

The functionalized nanofibers can be used in the field of adsorption of heavy metal ions and dyes from the waste water, affinity membrane and so on. There are several methods reported in literature that have been used to produce nanosize fibers. They are drawing, template synthesis, phase separation, self-assembly, electrospinning etc. Usefulness of above methods is restricted by combination of narrow material ranges, high costs and low production rates. Among the above nanofiber synthetic method electrospinning is a simple, convenient and low cost process that can produce ultrafine continuous fibers of many polymeric and ceramic materials [9,10].

2. EXPERIMENTAL SECTION

2.1 Materials and Methods

The following chemicals have been used for the synthesis and functionalization of Electrospun PAN membrane: Polyacrylonitrile (PAN) was obtained from Sigma Aldrich (US). Dimethylformamide (DMF), Sodium Hydroxide (NaOH), Hydrochloric acid (HCl), Ethylenediamine (EDA), Potassium chromate (K_2CrO_4), Malachite green (Dye) were purchased from Merck (INDIA). All chemicals were used without further purifications.

2.2 Synthesis of Electrospun PAN-nanofiber membrane

The 12 wt% solutions were prepared by dissolving (1.2gm) PAN in (8.8gm) DMF. Then mechanical stirring was done for 24 hrs. The prepared PAN solution was taken in a 5mL glass syringe. The feeding rate of the polymer solutions was 1 mL/h and a voltage of 13 kV was applied to the needle and the distance between the needle tip and collector was 12 cm. At a critical voltage, a jet of the polymer solution came out from the needle tip and was collected on the collector. When the solvent evaporated, a non-woven PAN fiber mat was formed.

2.3 Functionalization of PAN nanofibers by EDA and $NaHCO_3$

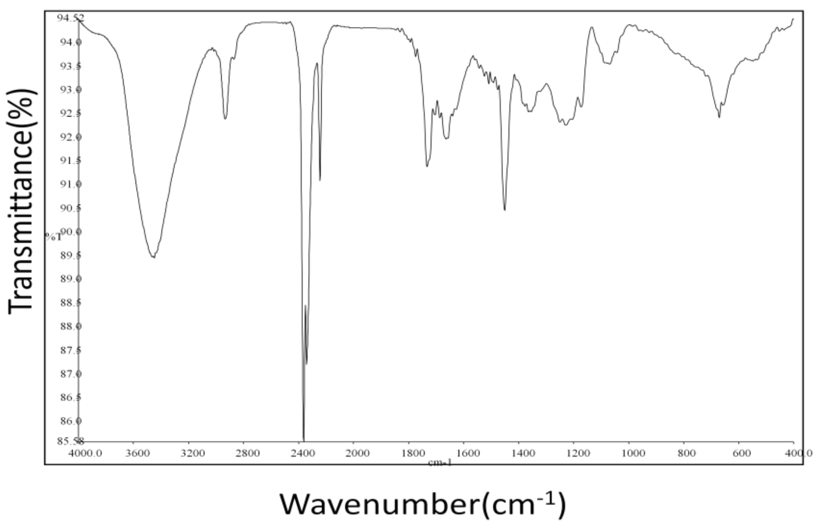
The obtained Electrospun PAN- nanofiber membrane was functionalized in two ways. (1) Functionalization of nitrile group of PAN into amide group by 10% solution of Ethylenediamine (EDA) and (2) Functionalization of nitrile group of PAN into carbonyl group by 10% solution of Sodium bicarbonate.

2.4 Adsorption experiments of modified PAN membrane by Batch process

We have used funtionlized PAN/EDA membrane for removal of hexavalent Chromium Cr(VI) and PAN/$NaHCO_3$-membrane for removal of Malechite Green(MG) dye from aqueous system. The effect of contact time on the adsorption of Cr (VI) on PAN/ EDA nanofiber the time variation was done with 30 min, 1 hr and 2 hrs by taking 0.1 gm of adsorbent and 10 ml of 10 ppm K_2CrO_4 solution. The effect of contact time, conc. and pH on the adsorption of Malachite Green (dye) on PAN/ $NaHCO_3$ were studied by 0.01 gm of adsorbent and 20 ml of 100 ppm Malachite Green (dye) solution.

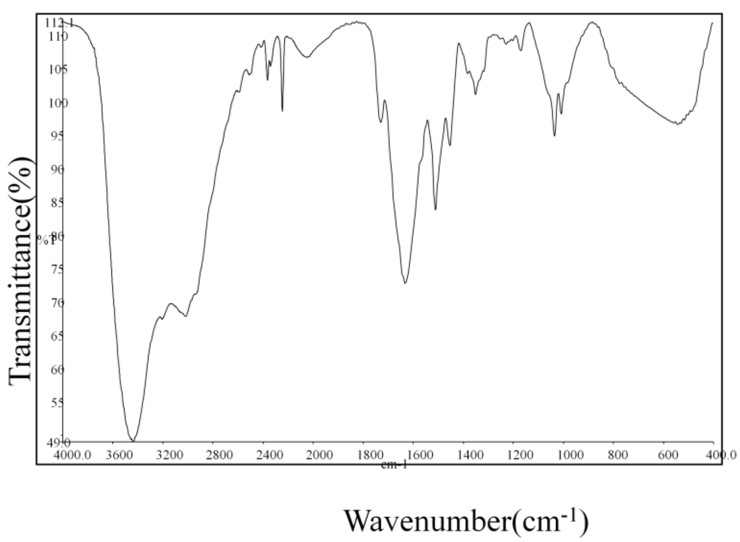
3. RESULTS AND DISCUSSIONS

3.1 Characterization of Electrospun Nanofibers by IR spectroscopy



Mode of Vibration	Peak position
(-CH_2-) stretching	3348 cm^{-1}
(-CN-) stretching	2242 cm^{-1}
(-CH_2-) bending	1450 cm^{-1}

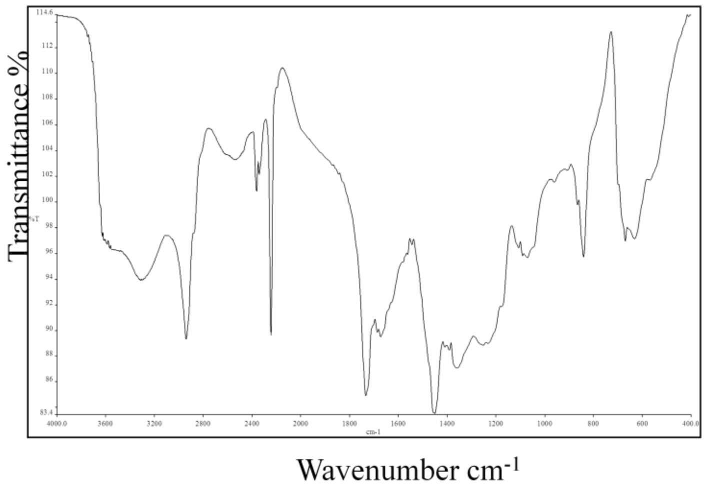
Fig 1.FTIR spectrum of Electrospun PAN nanofiber



Mode of Vibration	Peak position
(-NH-) stretching	3522 cm^{-1}
(-CO-) stretching	1677 cm^{-1}
(-CN-) stretching	2242 cm^{-1}
(-CH_2-) bending	1465 cm^{-1}

Fig 2. FTIR spectrum of Electrospun PAN nanofiber functionalized with EDA

It is observed from the fig 2.that the high intense peak of –CN at 2242 cm^{-1} in case of PAN membrane is reduced and subsequently reappearance of –CO- peak at 1677 cm^{-1} indicates the formation of amide functional group. There is also presence of –NH- stretching peak at 3522cm^{-1} was observed. This result indicates the conversion of –CN group of PAN membrane into -CO-NH- functional group.



Mode of Vibration	Peak position
(-CO-) stretching	1735 cm^{-1}
(-CN-) stretching	2242 cm^{-1}
(-CH_2-) stretching	3000 cm^{-1}
(-CH_2-) bending	1456 cm^{-1}

Fig 3. FTIR spectrum of Electrospun PAN nanofiber functionalized with $NaHCO_3$

3.2 Characterization of functionalized Electrospun PAN Nanofibers by SEM-EDAX technique

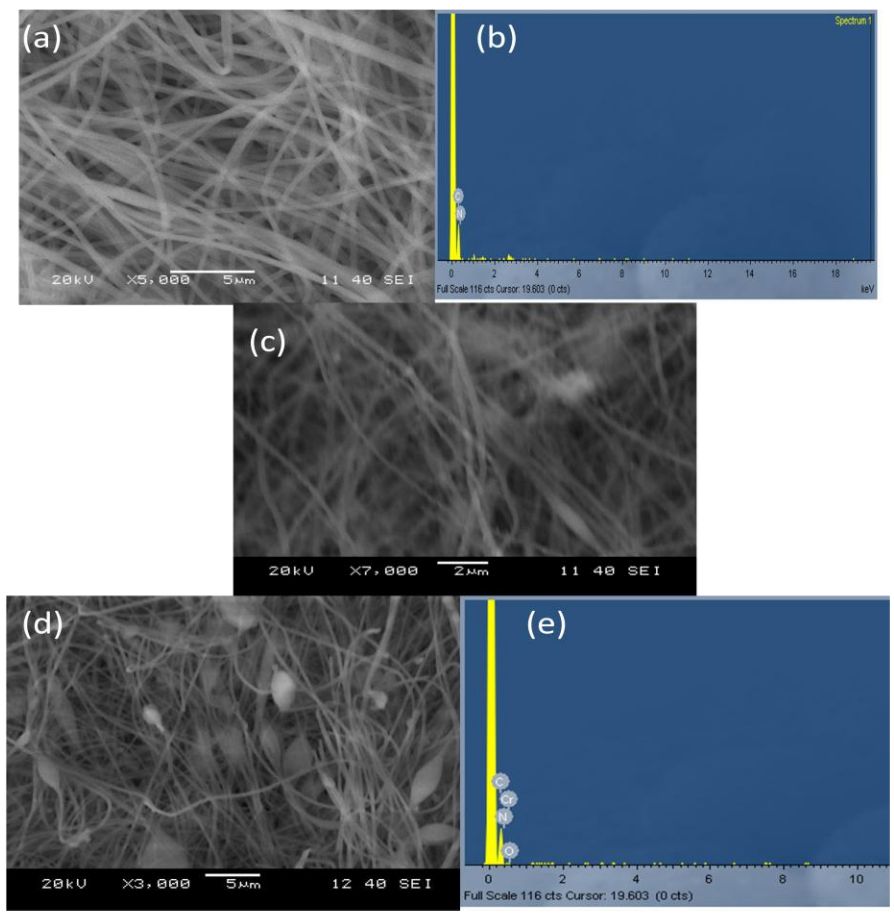


Fig4. (a) SEM image of PAN, (b) EDAX of PAN, (c) SEM image of functionalized PAN/EDA, (d) after adsorption, (e) EDAX after adsorption

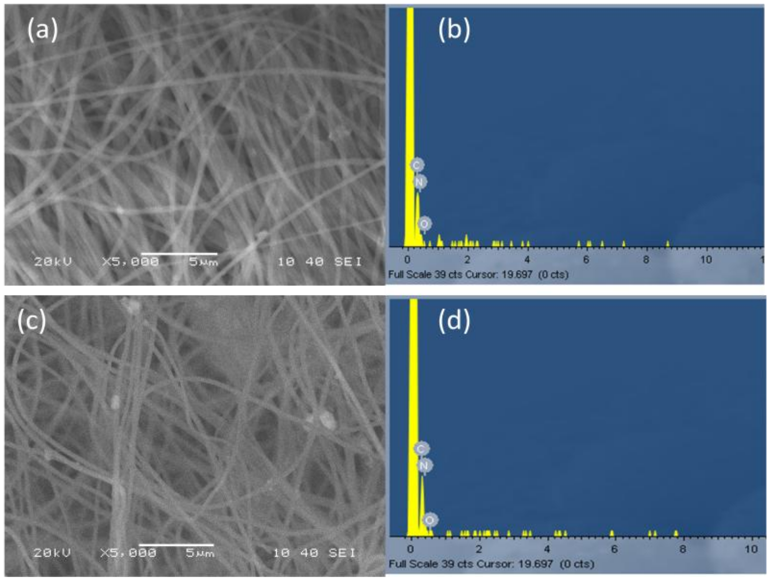


Fig5. (a) SEM image of functionalized PAN/NaHCO$_3$ membrane, (b) EDAX of functionalized PAN/NaHCO$_3$ membrane, (c) after adsorption, (e) EDAX after adsorption

3.3 ADSORPTION EXPERIMENTS

Effect of Time

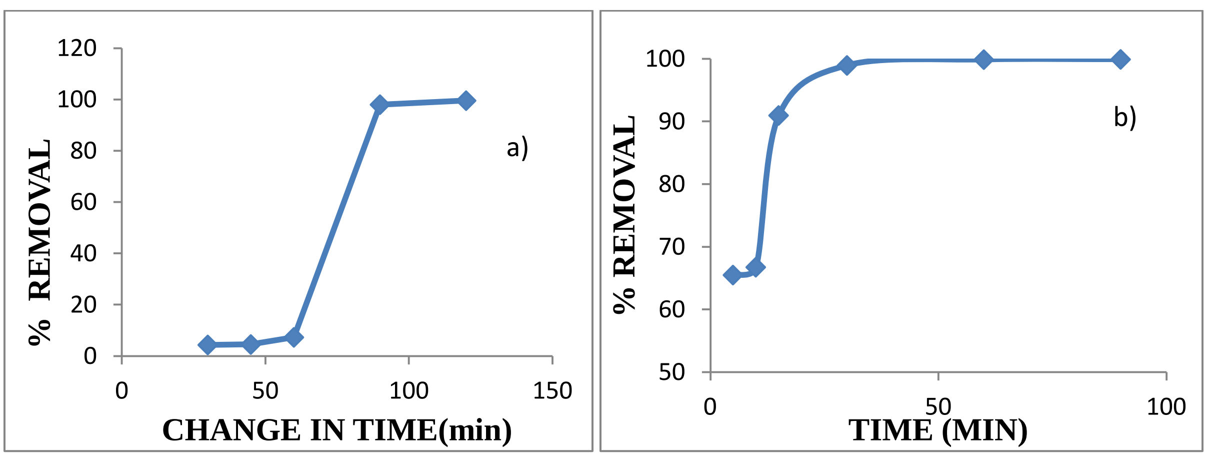


Fig6. (a) Adsorption of Cr (VI) on the surface of the PAN membrane functionalized with EDA with variation of time, Fig. (b) Adsorption of Dye (Malachite green) on the surface of the PAN membrane functionalized with NaHCO$_3$ with variation of time

Fig 6(a) shows the effect of contact time on the adsorption behavior of the Electrospun PAN membrane functionalized with Ethylenediamine. It has been shown that adsorption increased with increase in contact time. Maximum removal of Cr (VI) was found to be 99% at 2 hour of contact time.

Fig 6(b) shows the effect of contact time on the adsorption behaviour of the Electrospun PAN membrane functionalized with Sodium bicarbonate. In this case also adsorption increased with increasing contact time. Maximum removal of Malachite Green was found to be 99% at 30 min of contact time.

Effect of P^H and Conc.

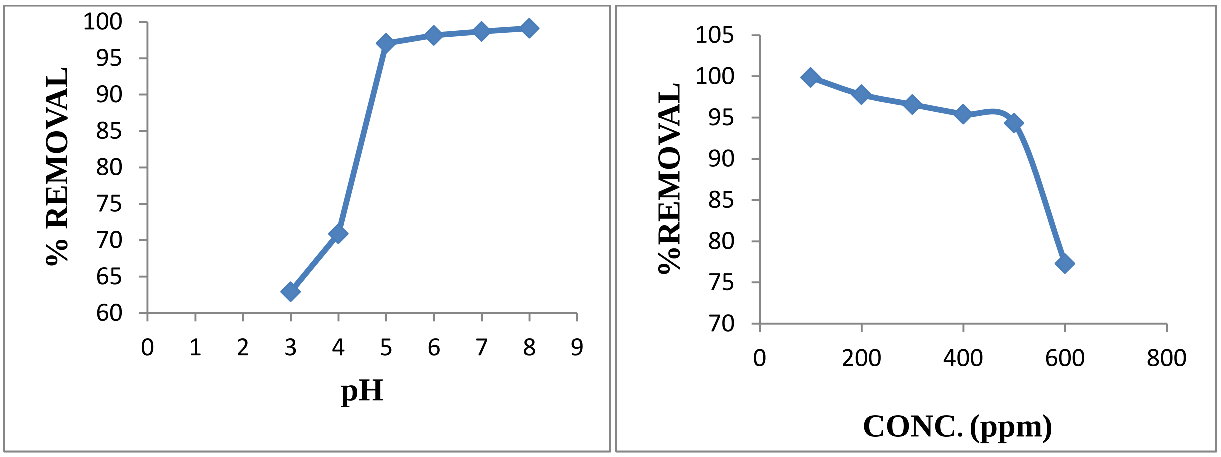


Fig 7(a), (b) Adsorption of Dye (Malachite green) on the surface of the PAN membrane functionalized with $NaHCO_3$ with variation of pH and variation of conc.

From the fig 7(a), it is observed that, at the low pH small amount of dye could be absorbed on to the functionalized PAN membrane. But with the increasing pH, the removal percentage of dye has been increased sharply, the optimum pH value for maximum removal of Malachite Green is found to be pH- 5.

It is observed from the fig 7(b) that, at conc. of 100 ppm, the percentage removal of dye is around 99% and with increasing conc. the % removal of dye has been decreased. From 500 ppm to 600 ppm, there is a sharp decrease in the removal percentage of dye. It is due to the saturation and non availability of adsorption site.

3.4 ADSORPTION KINETICS

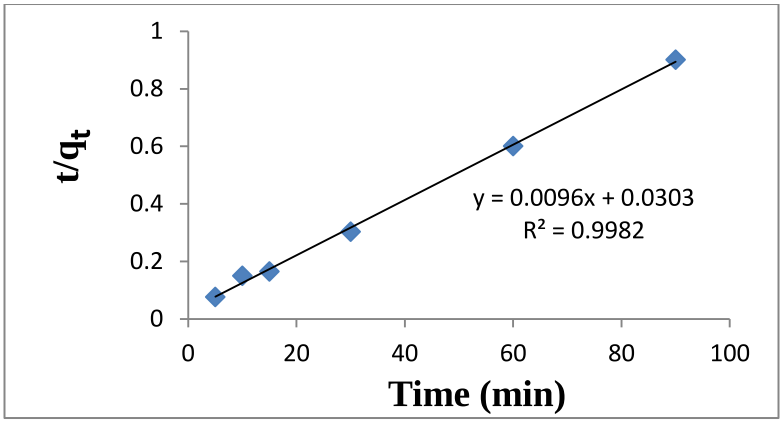


Fig 8. Pseudo-second-order Kinetic model

From the above fig. it is observed that the adsorption of Malachite Green (dye) on PAN/ $NaHCO_3$ follows Pseudo Second Order Kinetics. The value of R^2 (regression coefficient) is found to be 0.998.

4. CONCLUSION

- Electrospun PAN nanofiber Membrane has been synthesized successfully by Electrospinning method.
- Surface modification Electrospun PAN nanofiber Membrane have been done successfully with Ethylene diamine, Sodium bicarbonate, which is confirmed from IR spectroscopy, CHNX analysis, SEM images and SEM-EDAX analysis.
- Adsorption study of Cr (VI) and Malachite Green (Dye) from aqueous solution was done by Electrospun PAN membrane functionalized with EDA and $NaHCO_3$using UV- visible spectroscopy.
- The effect of contact time, pH and conc. on the adsorption of Cr (VI) and Malachite Green (Dye) on the functionalized Electrospun PAN membrane has also been studied.
- The adsorption of Malachite Green on Electrospun PAN membrane functionalized with $NaHCO_3$ fitted well with the Langmuir equation and follows Pseudo Second Order Kinetics.

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