Development of a Nanocomposite Membrane for Organic Dye Removal

Maadri A. Pathirana
Department of Textile and Apparel Engineering
University of Moratuwa
Sri Lanka
maadrip@uom.lk

Nethmi S.L. Dissanayake
Department of Textile and Apparel Engineering
University of Moratuwa
Sri Lanka
nethmidissanayake26@gmail.com

Gayani K. Nandasiri
Department of Textile and Apparel Engineering
University of Moratuwa
Sri Lanka
gayanin@uom.lk

Nandula D. Wanasekara
Department of Textile and Apparel Engineering
University of Moratuwa
Sri Lanka
nandulad@uom.lk

Boris Mahltig
Department of Textile and Clothing Technology
Hochschule Niederrhein
Germany
Boris.Mahltig@hs-niederrhein.de

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I. INTRODUCTION

Contaminated wastewater poses a significant threat to both the ecosystem and human health. The annual production of commercial dyes exceeds $7x10^5$ tonnes, with the textile industry being responsible for two-thirds of the consumption [1]. Moreover, an estimated 10-20% of the manufactured dye is annually released into the effluent stream [2]. Previous literature indicates that adsorption offers promising solutions to organic dye removal owing to its simplicity and cost-effectiveness. Adsorption is fundamentally defined as the process through which ions, atoms and molecules are retained on solid surfaces via physical or chemical bonding. The literature extensively covers adsorbents designed for individual removal of either anionic or cationic dyes. However, research on techniques for simultaneous removal of both types of dyes is limited. As anionic and cationic dye molecules contain charges, adsorption can initiate through the formation of electrostatic bonding.

Methylene blue (MB), a toxic and non-degradable cationic dye commonly found in textile effluent streams, poses challenges for removal due to its strong interactions with water molecules. Similarly, Congo red (CR), a benzene-based azoic anionic dye used in the textile industry, undergoes reductive cleavage, producing benzidine, a known human mutagen and carcinogen, leading to health concerns such as respiratory problems, skin and eye irritation.

Nanotechnology has led to significant research interest in using electrospun polymeric nanofibers (EPNs) as effective adsorbents for organic contaminant removal in wastewater treatment. Polyacrylonitrile (PAN) is commonly used for fabricating EPNs due to its excellent thermal and mechanical properties. Modified PAN nanofibers with amino groups, achieved through ethylenediamine (EDA) functionalization, exhibited the highest adsorption capacity for congo red dye (130 mg/g) [3]. Among various adsorbents for methylene blue, graphene oxide stands out for its high surface area, two-dimensional structure, and oxygen-containing functional groups enabling strong electrostatic interactions with cationic dyes.

This study explores the possibility of employing two novel nanocomposite membranes for the simultaneous removal of methylene blue and congo red dyes. The membranes include a dip-coated chitosan-graphene oxide (Ch-GO) PAN-EDA electrospun membrane and a Ch-GO electrosprayed PAN-EDA electrospun membrane.

II. MATERIALS AND METHODS

A. Materials

Polyacrylonitrile powder (Mw = 150000) was purchased from Shandong Natural Micron Pharm Tech Co., LTD, China. Chitosan was synthesized using shrimp shells retrieved from domestic waste. Graphene oxide was synthesized with graphite powder purchased from Neochem International (Pvt) Ltd. Hydrogen chloride (HCl, 37%), Sodium Hydroxide Pallets (NaOH, 97%), Dimethyl Formamide (DMF, 99.8%), Ethylene Diamine (EDA, 99%), Acetic acid (Glacial, 100%), Phosphoric acid (H3PO4, 85%), Sulphuric acid (H2SO4, 99%), Potassium permanganate (KMnO4, 99.9%), Hydrogen peroxide (H2O2, 30%), and Ethanol (C2H5OH, 99%) were purchased from Sigma Aldrich. All the chemicals were used without any further purification.

B. Methodology

Chitosan extraction from dried shrimp shell powder followed three steps: Demineralization, Deproteinization, and Deacetylation. Graphene oxide (GO) was synthesized via a modified Hummers method. A Ch-GO solution was prepared by dispersing 0.5% (w/v) GO in 1% acetic acid, followed by adding 2% chitosan solution in 4% acetic acid and ultrasonication. For PAN electrospun nanofiber mats, a 10wt% PAN solution was electrospun using a syringe pump and a 20KV voltage. Functionalization with EDA involved treatment with NaOH, HCl, and a 10% EDA solution. One PAN-EDA membrane was dip-coated with Ch-GO and dried, while the other was electrosprayed with Ch-GO (0.5 ml/hr, 20 kV voltage, and 12 cm tip to collector distance).

C. Characterization

Surface morphology of nanofiber membranes was investigated using SEM (Zeiss Evo 18 Research SEM, Carl Zeiss Microscopy, USA). FTIR Spectroscopy (FTIR Bruker Vertex 80, Bruker Corporation, USA) determined the chemical structure and functional groups in the range of 4000 to 400 cm^−1. UV-Visible NIR Spectrometer (UV-3600, Shimadzu, Japan) was used for the absorbency study of Methylene Blue dye onto the nanofiber membranes. Wettability of the membranes was analyzed with the Drop Shape Analyzer (Kruss, Germany).

D. Adsorption Study

The equilibrium uptake capacity of the two nanofiber membranes was evaluated in batch mode. The experiments involved fixed amounts of adsorbent in sealed sample bottles with varying pH levels and initial dye concentrations. UV-vis spectroscopy was used to measure absorbance at the maximum absorption wavelengths (λ = 664 nm for methylene blue and λ = 497 nm for Congo red). The equilibrium uptake of both methylene blue and Congo red were calculated using the following equation.

$$Q_e = \frac{C_0 - C_e}{W} \times v \qquad (1)$$

where Q_e (mg/g) is the weight of dye adsorbed per unit mass of adsorbent, C_0 (mg/l) is the initial dye concentration, Ce (mg/l) is the residual amount of MB or CR, V(l) is the volume of the dye solution, and W(g) is the weight of the adsorbent.

III. RESULTS AND DISCUSSION

A. FTIR Analysis

According to the FTIR spectra results depicted in fig. 1(a), the blue shift of N-H bending from 1556 cm^{-1} of chitosan to 1536 cm^{-1} of Ch-GO indicates the occurrence of epoxy amin reaction, which confirms the synthesis of Ch-GO composite. In fig. 1 (b), the adsorptive bands at 3434, 1562, and 1690 cm^{-1} which correspond to the stretching vibration of amines, C=O stretch of the amide, and N-H bending vibration of the amide which are absent in the FTIR spectra of untreated PAN nanofibers, are present in PAN-EDA, which ultimately confirms the amide formation in PAN-EDA.

B. SEM Results

As per the results depicted by the SEM images, PAN nanofibers (fig. 1 (e)) appear to have smooth surface with an average diameter of 265 nm, while in the functionalized (fig. 1 (f)) PAN, the fibers appear swollen, with an average diameter of 349 nm, but the smooth morphology remains unchanged. In the Ch-GO dip coated nanofiber membrane (fig. 1 (g)), the diameter seems to have increased further (diameter of 394 nm) which may be due to the layered thickness if the Ch-GO coating. The smooth surface of the PAN membrane appears to be converted to a rougher surface following the immersion coating. An agglomerated particle of size 2.1µm can be seen attached to the PAN fibers. In the SEM image of the Ch-GO electrosprayed nanofiber membrane (fig. 1 (c)), an agglomerated particle of 3.2µm can be seen attached to the PAN fibers which may have been due to the aggregation of GO particles. This might have been due to the due to the logistics involved in electrospraying, i.e., time taken to take the sonicated sample from bath sonicator to the electrospinning unit the and the preparatory procedure involved in electrospraying.

C. Contact Angle Measurements

As per the results obtained from contact angle measurements, as depicted in fig. 1(d), the static contact angle of PAN electrospun membrane measured using the sessile drop method was 68° and subsequent to surface modifications the fabricated EPNs demonstrated perfect wettability (fig. 1(h) and fig. 1(i)). As reported in literature the hydrophilicity of an EPN will depend on the polarity, homogeneity, and layer thickness. The significant improvement in the surface wettability of the Ch-GO dip coated and Ch-GO electrosprayed PAN-EDA electrospun nanofiber membranes can be attributed to its successful coating of the top tier. This may contribute favorably to dye adsorption capacity of fabricated membranes.

D. Adsorption Study

Absorption measurements were carried out at λ =664nm for MB and λ = 497 nm for CR, and linear calibration curves for MB (Figure 11 (a)), and CR (Figure 11 (b)), absorbance at variable concentration were obtained

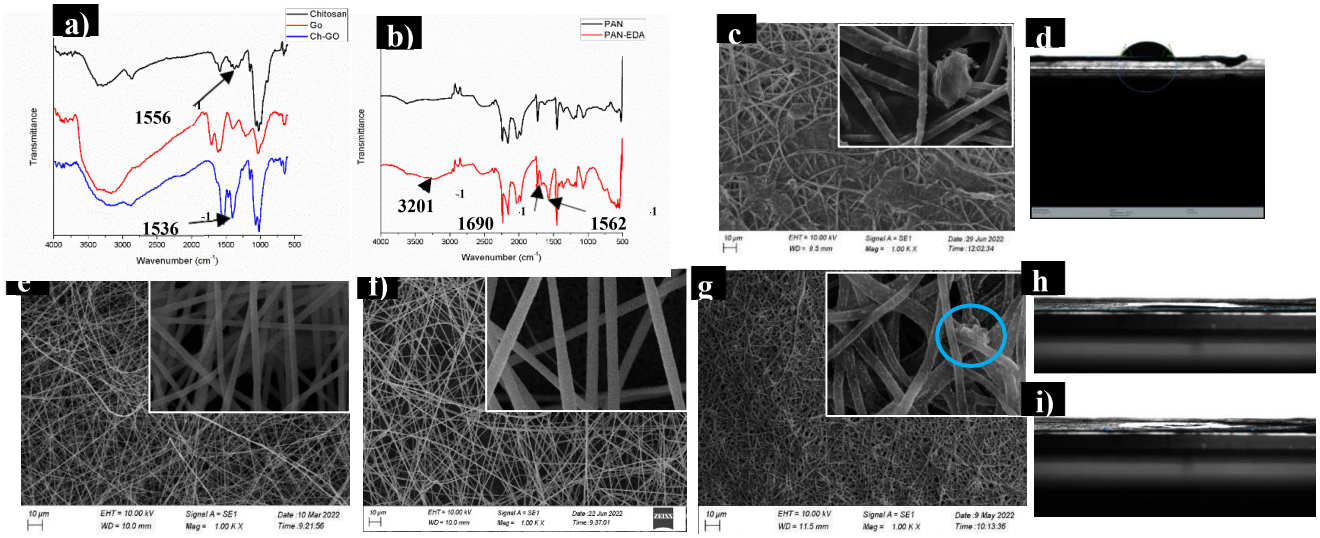

Fig. 1. a) FTIR spectra of chitosan, GO and Ch-GO, b) FTIR spectra of PAN, PAN- EDA c) SEM image of Ch-GO electrosprayed PAN-EDA nanofibers, d) Static contact angle of PAN nanofiber, e) SEM image of PAN nanofibers, f)SEM image of PAN-EDA nanofibers, g) SEM image of Ch-GO dip coated PAN-EDA nanofibers, h) Static contact angle of SEM image of Ch-GO dip coated PAN-EDA nanofibers, i) Static contact angle of SEM image of Ch-GO electrosprayed PAN-EDA nanofibers

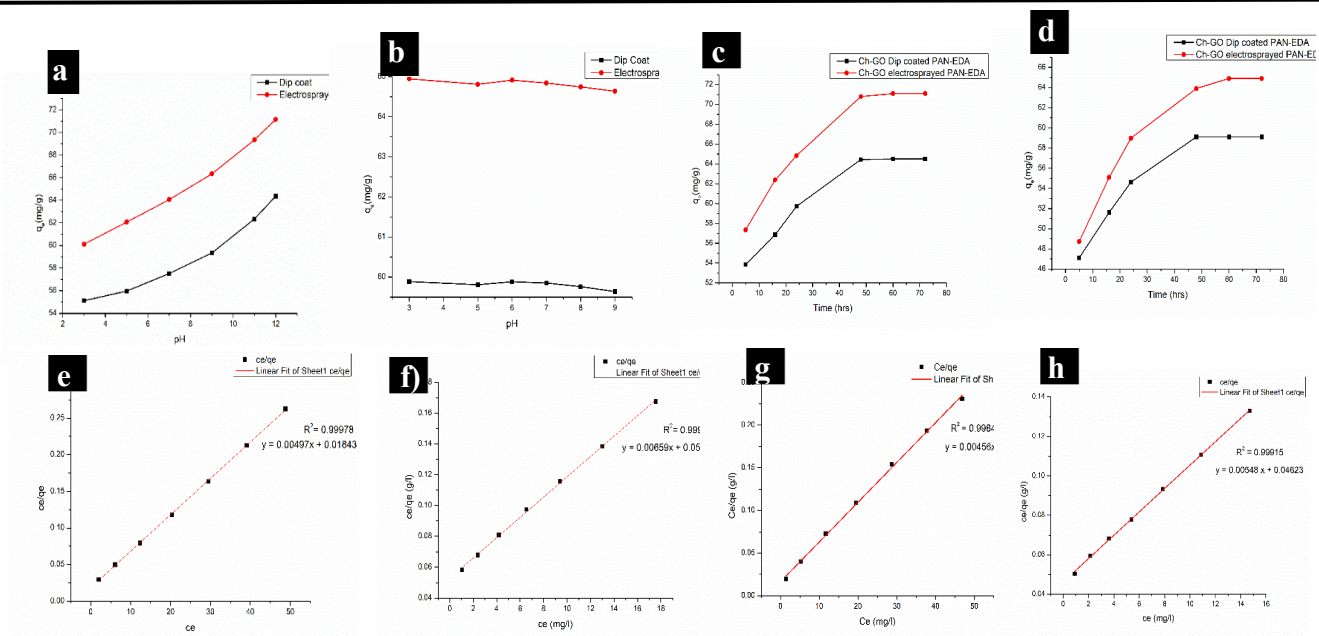

Fig. 2. a) Adsorption capacity of MB as a function of pH b) Adsorption capacity of CR as a function of pH, c) Adsorption capacity of MB as a function of contact time, d) Adsorption capacity of CR as a function of contact time, e) Langmuir isotherm model for MB related to the dip coated membrane, f) Langmuir isotherm model for CR related to the dip coated membrane, g) Langmuir isotherm model for MB related to the electrosprayed membrane, h)

As depicted in fig. 2 (a), the adsorption of MB on to the fabricated membranes is favorable in basic pH mediums which can be attributed to the to the increase in surface ionization of carboxyl groups decorated on GO surfaces, whereas the converse is true for the adsorption of CR (fig. 2 (b)). In low pH levels, the amide group undergoes protonation increasing the electrostatic attraction bonds with the anionic dye. Moreover, it can also be deduced from fig. 2 (c) and fig. 2 (d) that a sufficient contact time is required to reach equilibrium and as per the results given in the graph, a duration of 48 hours was required to achieve equilibrium.

Table 1 depicts the results of Langmuir and Freundlich models where the substrate 1 corresponds to the Ch-GO dip Coated PAN-EDA membrane and the substrate 2 refers to the Ch-GO electrosprayed PAN-EDA membrane. Based on the Langmuir isotherm plots shown in Fig. 2(e) to Fig. 2(f) and the data from Table 1, the high correlation coefficients of the Langmuir model for both MB and CR suggest monolayer homogeneous adsorption. The calculated maximum adsorption capacities (qmax) for MB and CR onto the dip-coated membranes are 201 mg/g and 152 mg/g, respectively. A similar conclusion can be deduced for the electrosprayed membrane with maximum adsorption capacities of 219 mg/g for MB and 182 mg/g for CR. The difference in the adsorption capacities can be attributed to the different coating methods adopted for the two membranes, with the electrospraying technique imparting a higher surface area for dye adsorption.

This adsorption capacity of both membranes exceeds that of the recent adsorbent developed by Patel and Hota [3] for CR, the reason for which can be attributed to the attributed to the presence of the chitosan top coating which accommodates additional protonated amino sites for anionic dye removal. Moreover, both adsorbents exhibit superior adsorption capacity to other carbon-based nanomaterials which can be due to the enhancement in adsorption capacity imparted by the oxygen containing functional groups on GO distributed over a large surface area. The adsorption capacity for MB of the two membranes significantly exceeds that of raw chitosan and is only slightly lower than GO powder.

Table I Results of Langmuir and Freundlich Isotherms

	Dye	Langmuir Isotherm			Freundlich Isotherm		
		q_{max} (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2
1	MB	201.20	0.26967	0.99978	62.2	3.293	0.89948
	CR	151.75	0.00035	0.99904	19.4	3.084	0.98049
2	MB	219.3	0.27788	0.99846	74.3	3.588	0.94099
	CR	182.48	0.00025	0.99915	21.2	1.529	0.98317

IV. Conclusion

As per the results extracted from Langmuir isotherm modeling, the dip-coated nanocomposite membrane adsorbed 201 mg/g of methylene blue and 152 mg/g of congo red, whereas the electrosprayed nanocomposite membrane exhibited even higher capacities: 219 mg/g for methylene blue and 182 mg/g for congo red, surpassing most reported adsorbents. This study's proposed adsorbent shows promise for advancing wastewater treatment. Future research can focus on improving the mechanical strength, reusability, regeneration, and durability of electrospun EPN membranes, thus enhancing scalability of the adsorbents.

V. References

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