Development of a PAN, Chitosan and MMT based Nanofibrous Membrane to Remove Chromium and Lead Heavy Metal Ions from Textile Dye Effluent

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Keywords— electrospinning, montmorillonite, chitosan, polyacrylonitrile, adsorption

I. INTRODUCTION

Water pollution is a growing global concern, with textile industries significantly contributing due to their high water consumption and the release of harmful pollutants. An average textile factory consumes 1.6 million liters of water daily, generating wastewater containing hazardous chemicals, including heavy metals like lead (Pb) and chromium (Cr) [1]. These metals, often released during textile processes such as dyeing and finishing, are toxic to the environment and human health. Lead exposure can cause cancer, birth defects, and neurological disorders, while chromium (especially in its hexavalent form, Cr^{6+}) is mutagenic and linked to carcinogenicity and stomach ailments [2]. Due to these risks, the World Health Organization (WHO) recommends maximum permissible limits for heavy metals in wastewater, setting the limit at 0.01 ppm for Pb^{2+} and 0.05 ppm for Cr^{6+} [3].

The treatment of wastewater containing heavy metals like Pb^{2+} and Cr^{6+} is crucial, with various methods being explored, including ion exchange, chemical precipitation, and biological techniques. However, adsorption is favored for its versatility, cost-effectiveness, and efficiency. Nanofiber adsorbents, particularly electrospun nanofiber membranes, offer advantages due to their high porosity, variable pore sizes, and large surface area [4]. The choice of materials, especially the combination of natural polymers like chitosan with synthetic polymers such as polyacrylonitrile (PAN), significantly impacts adsorption capacity [5]. Chitosan, known for its non-toxicity, biodegradability, and ability to chelate metal ions, is widely used in heavy metal remediation [6]. Magnetic nanoparticles further enhance the performance of chitosan-based adsorbents, adding mechanical strength [7]. PAN, known for its thermal stability and chemical resistance, is commonly used in nanofiber applications, and research is ongoing into chitosan-PAN composites for improved adsorption [8].

Natural clay minerals, particularly montmorillonite (MMT), are being explored for their inherent adsorption capabilities in water treatment, thanks to their negatively charged layered structure, high porosity, and large surface area. MMT's exchangeable cations enable effective adsorption of positively charged heavy metal ions via electrostatic attraction and ion exchange [9]. In Sri Lanka, where MMT is abundant, research has focused on its extraction and application, though its potential in electrospun nanomembranes for heavy metal remediation remains underexplored [10]. To enhance MMT's adsorption capacity, modifications such as carbonization—adding organic materials to create a carbon layer—are used [11]. Carbonized materials like activated carbon and biochar are known for their heavy metal remediation properties, though the specific use of carbonized MMT in this context has not been widely studied.

This study aims to develop an electrospun nanomembrane using a combination of PAN, magnetic chitosan, and carbonized montmorillonite (MMT) from Sri Lankan clay deposits to address the gap in research on heavy metal remediation. While carbonization of MMT and its adsorption capabilities have been explored, their application in nanomembranes for heavy metal removal remains under-researched. The study seeks to evaluate the effectiveness of this unique composite membrane for removing Pb^{2+} and Cr^{6+} from wastewater.

II. MATERIALS AND METHODS

A. Material Extraction

In this research, polyacrylonitrile (PAN) powder was obtained from Merck, Germany, and fresh tiger shrimp was sourced from the local market in Negombo, Sri Lanka, to extract chitosan. The shrimp heads and skins were separated, thoroughly washed, and ground using a mortar and pestle. The ground shrimp shells were placed in polyethylene bags at room temperature (26°C) for 24 hours to allow partial autolysis. Chitosan extraction followed three main steps: demineralization, deproteinization, and deacetylation, based on the method by Hossain et al. [12].

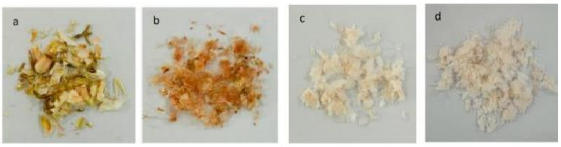

Fig. 1. (a) Raw Shrimp, (b) Demineralized Sample, (c) Deproteinized Sample (chitin), and (d) Deacetylated Sample

The process began with demineralization, which removed inorganic impurities like calcium carbonate and calcium phosphate from dried shrimp shell powder by treating it with 1M HCl at a 1:16 (w/v) ratio for 24 hours, followed by washing until neutral pH was achieved. Next, deproteinization separated chitin from proteins by treating the demineralized powder with 2M NaOH for 48 hours, with subsequent

washing. The resulting chitin was dried and weighed. Finally, deacetylation converted chitin into chitosan by treating it with 48% NaOH for 48 hours, followed by filtering, neutralizing, washing, and drying to obtain the final chitosan product.

B. *Preparation of Magnetic Chitosan*

Fe_3O_4 magnetic nanoparticles were synthesized using the co-precipitation method. A solution of $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ was dissolved in deionized water and stirred magnetically. While stirring, a 3M ammonium hydroxide (NH_4OH) solution was gradually added drop by drop, forming a black precipitate. The precipitate was then washed with deionized water to remove any residual alkali salts and separated by decantation. The Fe_3O_4 particles were redispersed in deionized water and freeze-dried for further use.

Covalent cross-linking of the magnetic chitosan composite (Fe_3O_4-CS) was carried out using glutaraldehyde as a cross-linking agent. Glutaraldehyde reacts with the primary amine groups on chitosan and the hydroxyl groups on magnetic nanoparticles to form stable covalent bonds, anchoring chitosan onto the Fe_3O_4 particles. First, a 1% chitosan solution was prepared by dissolving 1g of chitosan in 1 wt.% acetic acid. Then synthesized magnetic nanoparticles were dispersed in chitosan solution using ultrasonic irradiation. The suspension was stirred at 40°C while adding glutaraldehyde dropwise. After stirring for 4 hours, the black product was oven-dried at 60°C for 12 hours.

C. *Carbonization of Montmorillonite*

Carbonization is a process where organic materials/carbon sources are heated in a low-oxygen or oxygen-free environment, leading to the removal of volatile components, and leaving behind a porous carbon-rich residue on top of the clay material base. In the below methodology Glycerol (carbon source) in the presence of H_2SO_4 as catalyst was carbonized on a montmorillonite surface. Glycerol, H_2SO_4 , and montmorillonite was combined in a beaker. The mixture was then subjected to gradual heating in a vacuum oven until reaching 240°C. The MMT/glycerol samples were then held at this temperature for an additional 1 hour under inert atmospheric conditions. The resulting samples exhibited a black color, indicative of the presence of carbonaceous material.

D. *Electrospinning of the Membrane*

The preparation of electrospun composite nanofibers began by dissolving 3 grams of Polyacrylonitrile (PAN) powder in 27 ml of Dimethylformamide (DMF) through magnetic stirring for 24 hours at room temperature. Once the PAN powder was fully dissolved, 2 wt.% of carbonized Montmorillonite (MMT) powder and 2 wt.% of magnetic chitosan were added to the polymer solution. This mixture was then stirred for an additional 3 hours. To ensure the complete dispersion of MMT and magnetic chitosan in the spinning solution, the mixture was ultrasonicated for 15 minutes before electrospinning. The final solution was then loaded into a 10 ml syringe with a diameter of 1.5 cm and placed into the electrospinning setup. The solution was subjected to the electrospinning process under a positive voltage of 20 kV, with a controlled flow rate set at 0.07 mL/ min at a temperature of 20°C. The electrospun fibers were collected onto an aluminium foil collector, maintaining a working distance of 7 cm.

E. *Regeneration Studies*

Regeneration studies were conducted to evaluate the reusability of the PAN/Carbonized MMT/Magnetic Chitosan membrane for cost-effective wastewater treatment. The membrane, after adsorbing Cr^{6+} and Pb^{2+} ions, was treated with a 0.01 M NaOH solution and stirred for two hours at 150 rpm to desorb the heavy metal ions. It was then thoroughly rinsed with deionized water and dried at 60°C for one hour. The membrane was subsequently reused for another adsorption cycle, demonstrating its regeneration capacity and potential for repeated use in heavy metal ion removal.

III. Results and Discussion

A. *FTIR – Analysis of Magnetic Chitosan*

The FT-IR spectra confirm the successful synthesis and combination of Fe_3O_4 magnetic nanoparticles with chitosan in the formation of magnetic chitosan. The Fe_3O_4 nanoparticles exhibit characteristic peaks at 566 cm^{-1} (Fe-O stretching) and bands at 3333 cm^{-1} and 1635 cm^{-1} (O-H stretching). In the magnetic chitosan composite, the increased intensity of the peak around 3300 cm^{-1} suggests more active hydroxyl groups, and the presence of a peak at 571 cm^{-1} reaffirms the Fe_3O_4 structure within the composite. These findings align with previous literature, confirming the structural integrity of the synthesized materials.

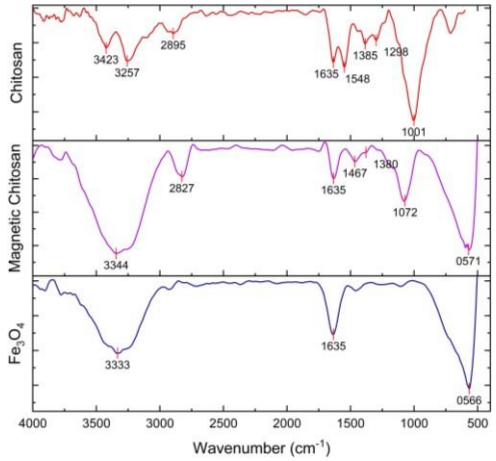

Fig. 2. FTIR spectra of Magnetic Chitosan (left) & Synthesized Chitin and Chitosan

B. *SEM Analysis of Carbonized MMT*

The examination of the montmorillonite clay surface morphology was conducted through scanning electron microscopy (SEM). Prior to carbonization, natural clay displayed irregular surfaces and layers resembling flakes, as illustrated in Fig. 3 (left). Subsequent to the carbonization process, depicted in Fig. 3 (Right), at the same magnification, the surface exhibited a higher roughness in texture, signifying an increase in the flake structure. This observation implies that the carbonization process has caused a higher surface area, potentially leading to enhanced adsorption capacity.

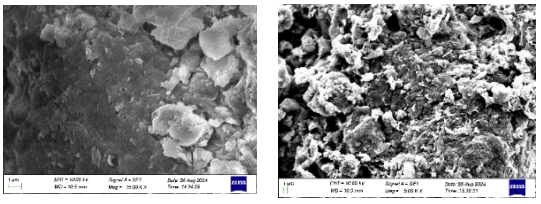

Fig. 3. SEM images of Normal MMT (left) and Carbonized MMT (Right)

C. SEM and EDAX Analysis of PAN/Carbonized MMT/Magnetic CS membrane

The SEM analysis of the PAN/Carbonized MMT/Magnetic Chitosan nanofiber membrane confirms the successful incorporation of MMT particles within the nanofibrous structure. These particles are well-embedded on the fibers, indicating strong interaction with the nanofibrous matrix, which is likely to enhance the membrane's adsorption capabilities. The nanofibers have an average diameter of 468.512 nm, as measured using ImageJ software. The synthesized magnetic nanoparticles were tested for their size and the average particle size was approximately 50 nm.

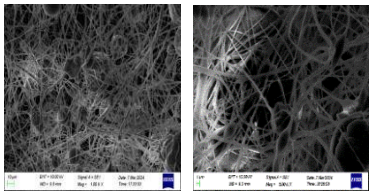

Fig. 4. SEM images of electrospun nanomembrane

D. Adsorption Experiments

In this study, the adsorption behavior of Cr^{6+} and Pb^{2+} ions on a PAN/Carbonized MMT/Magnetic Chitosan membrane were investigated using a UV-Spectrophotometer. Adsorption capacities were calculated as 83.47 mg/g for Cr^{6+} and 65.06 mg/g for Pb^{2+}, revealing that the membrane has a higher adsorption capacity for Cr^{6+} compared to Pb^{2+}, demonstrating its effectiveness in heavy metal removal.

E. Regeneration Studies

The PAN/Carbonized MMT/Magnetic CS membrane showed a gradual decline in removal efficiency for Cr^{6+} and Pb^{2+} over five adsorption-desorption cycles. Initially, the membrane removed 65.29% of Cr^{6+} and 55.76% of Pb^{2+}, but by the fifth cycle, these values decreased to 53.43% and 48.30%, respectively. Despite the reduction, the drop in performance was not significant, indicating the membrane remains effective for repeated use.

F. Adsorption Studies under different pH and Temperatures

The adsorption behavior of Cr^{6+} and Pb^{2+} ions on the PAN/Carbonized MMT/Magnetic CS membrane were studied over a pH range of 2 to 8. Pb^{2+} ions showed increased adsorption with rising pH, reaching saturation at higher pH levels, as reduced protonation minimized competition with H^+ ions. In contrast, Cr^{6+} ions exhibited higher adsorption at lower pH due to stronger electrostatic attraction to protonated membrane sites, but adsorption decreased at higher pH as these interactions weakened. The pH significantly influenced the ionization of functional groups on the membrane, affecting the electrostatic interactions between the metal ions and adsorption sites. The adsorption studies of PAN/Carbonized MMT/Magnetic CS membranes for Cr^{6+} and Pb^{2+} ions demonstrated that the equilibrium adsorption capacity increases with both rising initial concentrations and temperatures (298K, 308K, 318K). The higher temperatures enhance the kinetic energy of ions, promoting better diffusion and interaction with the membrane's active sites. Cr^{6+} adsorption showed a more pronounced temperature dependence compared to Pb^{2+}, likely due to differences in ionic radii, charge densities, and interactions with the membrane. This suggests that temperature control is especially important for optimizing Cr^{6+} adsorption efficiency.

IV. Conclusion

In conclusion, the PAN/Carbonized MMT/Magnetic Chitosan nanofibrous membrane shows excellent adsorption capacities of 65.06 mg/g for Pb^{2+} and 83.47 mg/g for Cr^{6+}. Initial removal efficiencies were 55.76% for Pb^{2+} and 65.29% for Cr^{6+}, though these declined to 48.30% and 53.43% by the fifth cycle. The integration of carbonized montmorillonite and magnetic chitosan enhances the membrane's structure and adsorption capacity. Additionally, the membrane demonstrated effective adsorption across different temperatures and pH values.

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