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Adsorption of reactive blue 19 as an anionic dye by PVA/CS/Triton X-100 electrospun nanofibers

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Abstract: Reactive dyes, due to their high molecular weight and aromatic structure, are considered more challenging pollutants than other dyes. They are highly soluble in water and are not easily removed through conventional treatment methods. The use of adsorbents to eliminate these dyes is a common approach. In this study, polyvinyl alcohol/chitosan (PVA/CS) nanofibers modified with Polyethyleneimine (PEI) were utilized as adsorbents for the removal of reactive dyes. Both polymers possess high hydrophilicity and biodegradability. The electrospinning technique, a common and cost-effective method, was employed for nanofiber fabrication. Additionally, Triton X-100 was used to facilitate the electrospinning process and enhance the quality of nanofibers.

Keywords: Dye adsorption, Polyethyleneimine (PEI), Chitosan (CS), Polyvinyl alcohol (PVA),

1. INTRODUCTION

The textile industry is one of the most important industries that is constantly advancing. The wastewater treatment of these industries is crucial due to the presence of thousands of different dyes and toxic substances. There are significant concerns regarding the presence of chemical compounds in the wastewater that exhibit high resistance to biological degradation [1,2]. Reactive Blue 19 is a dye belonging to the group of anthraquinone dyes, and it is one of the most commonly used textile dyes after azo dyes. Various methods have been employed to remove it, such as sonochemistry, photochemistry, the use of nanoparticles, and more. These methods are used to enhance the efficiency and application of wastewater treatment containing Reactive Blue 19 dyes [3,4].

The high cost, resistance to removal, and the potential for recontamination in the process of removing dyes from wastewater have posed significant challenges in the field of dye removal. In this study, the surface adsorption of Reactive Blue 19 dye using electrospun nanofibers functionalized with a surfactant has been investigated. This method offers an easy and common approach to address the challenges associated with dye removal [5]. Electrospinning is a simple and inexpensive method for producing nanofibers on a nanoscale and microscale. The fabrication of electrospun nanofibers is a common method for producing fibers with various applications in industries such as pharmaceuticals, membranes, medical bandages, and water purification [6,7]. This study utilizes a blend of two biodegradable natural polymers, polyvinyl alcohol (PVA) and chitosan, for the production of nanofibers. Both polymers are environmentally friendly and pose no risk of pollution. The inclusion of PVA alongside chitosan aids in the electrospinning process due to its high fiber receptivity. Additionally, Triton X-100

was used to create a more uniform surface and increase the viscosity of the polymer solution, facilitating the process [7-10].

In this work, we have chemically modified the surface of the PVA/CS/Triton X100 electrospinning the nanofibers matrix by using polyethyleneimine (PEI) to generate a positive charge on the nanofibers' surface. PEI was used as the functional compounds because of their abundant primary amine ($–NH_2$), secondary amine ($–NH^-$) groups [11-14].

2. MATERIALS AND METHODS

2.1 Materials

Glutaraldehyde (GA 50 % solution), Triton X-100, sodium carbonate (Na2CO3) (SigmaAldrich), Polyethyleneimine (PEI), Polyvinyl alcohol (PVA) (99 % Mw = 145 kDa), Acetic acid, Hydrochloric acid (HCl 37 %), Isopropyl Alcohol (Merck), Chitosan (high molecular, purity >97 %) (Azin Turkan).

2.2 Fabrication of electrospun PVA/CS/TRITON-X100 composite nanofibers To prepare the electrospinning solution, start by placing PVA 8 % w/v solution in DI water on a magnetic stirrer at a temperature of 60 °C for 12 hours to allow complete dissolution. In next step CS (Chitosan) 3 % w/v solution was prepared by dissolving in Acetic acid and DI water 7/3 on a stirrer for 6 hr. PVA and CS solution were mixed in order to prepare solution with PVA/CS volume ratios of 7/3 for 3 hours. After the solution has cooled down, Half of the solution separated and the other half Triton X-100 1 % v/v is added to the solution, and it is placed on a stirred at room temperature for 30 min.

2.3 Electrospinning process

The PVA/CS/Triton X-100 electrospinning solution was placed into a 6 mL syringe and pumped by flowing rate of 1 mlh^{-1}. the voltage DC power was 20 kV and the distance between the tip to collector is 15 cm and the electrospinning process continues for 3 hr. In the next step, electrospinning was used to fabricate PVA/CS nanofibers without Triton X-100 under the previous electrospray conditions. After that, both electrospun nanofibers was placed in an oven for 12 hours at a temperature of 35^0 C to fully volatilize the solvent.

2.4 Cross-linking of nanofiber membrane by GA

Glutaraldehyde (50 %) was dissolved in isopropyl alcohol with a volume percentage of 0.5 %, and HCl 0.4 % (HCL/GA v/v) was used as a catalyst. the isopropyl was used as the main crosslinking solvent because it will not lead to destroy of the morphology as a non-solvent of the PVA/CS/Triton X-100 composite nanofibers. Both nanofiber samples were immersed in a GA solution and kept for one hour to ensure complete cross-linking. Then, the nanofibers were placed inside an oven at a temperature of 60 °C for 4 hours to remove any remaining solvents also enhance the resistance of the nanofibers.

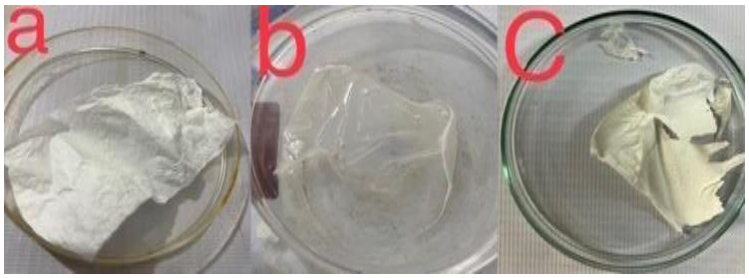

Figure 1. a) PVA/CS/Triton x100 nanofibers. b) Cross-linking by GA solution. c) Dried PVA/CS/Triton X100 nanofibers

2.5 Functionalization of nanofibers

Polyethyleneimine (PEI), which contains amine groups, was used to functionalize the nanofibers. To create a functionalized surface on the electrospun PVA/CS/Triton X-100 nanofibers, which were immersed in a solution containing 15 mL of PEI and 0.2 mL of sodium carbonate for 2 hours. Then, the functionalized nanofibers are washed three times with DI water to remove any excess materials completely. In the final step, the nanofibers are placed inside an oven at a temperature of 60 °C for 12 hours to dry them and ensure they have the necessary strength.

3. RESULTS AND DISCUSSION

The PVA/CS/Triton X-100 electrospun nanofibers were utilized as mass adsorbents for color removal from a solution. In this stage of the process, the adsorption capacity was evaluated based on pH and the duration of the study. (NaOH and HCL were used to adjust the pH of the solution.) The highest adsorption capacity was observed at pH < 3.

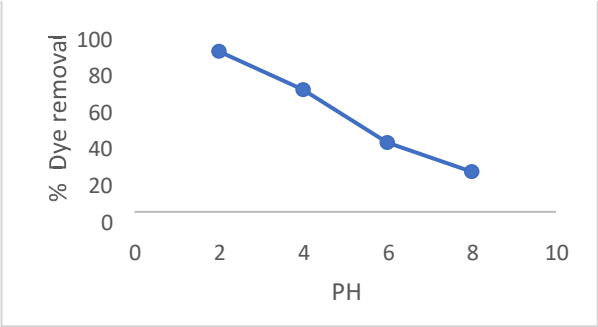

Figure 2. Dye removal % in different PH

Under these conditions, the amino groups ($-NH_2$) on the fiber mass become protonated and transformed into positively charged groups ($-NH_3^+$). This strong electrostatic attraction between the positively charged nanofibers ($-NH_3^+$) and the anionic color molecules (such as sulfonic acid groups) leads to the adsorption of the color molecules onto the adsorbent.

CONCLUSIONS

At higher pH values (alkaline conditions), the number of positively charged sites on the nanofiber mass will decrease. Figure 2 shows the variations in pH and its impact on color

removal. It also indicates that the highest percentage of color removal occurs at a pH close to 2 where more than 90 % color adsorption was observed.

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