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Synthesis, characterization and application of zinc augmented aminated PAN nanofibers towards decontamination of chemical and biological contaminants

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ABSTRACT

A novel amine functionalized Polyacrylonitrile (PAN) based electrospun nanofibers mat decorated with zinc (A/Zn/PAN) was synthesized, characterized and evaluated for the decontamination of chemical and biological contaminants. The loading capacity of the chromium (Cr (VI)) and congo red (CR) dye on A/Zn/PAN nanofiber mat were approximately 23 and 25 mg/g, respectively. Various adsorption parameters like pH, kinetics, dose rate were ascertained by using batch adsorption experiments. Using XPS studies a suitable mechanism has been proposed for the adsorption. The nanofiber mat was found to be effective in inhibiting the growth of *Escherichia coli*, and *Staphylococcus aureus* bacterial strains.

Introduction

At present, global existence of chemical and biological contaminants such as bacteria, dyes, and toxic metals ions, in water resources has increased environmental concern because of their adverse effects on living things including human health. The metal ions have high solubility in the water system, thereby, easily enter into the food chain and might accumulate in the body of living things [1]. The Congo red (CR) dye (Fig. 1) is a well known pollutant and considered to be cytoxic and carcinogenic in nature. The biological contamination such as *Eschericia coli* (*E. coli*), and *Staphylococcus aureus* (*S. aureus*) bacteria in the water bodies leads to acute and chronic health effects on human that causes various diseases mainly bacterial infection [2]. Therefore, there is a need to prepare an efficient as well as cost effective, newer or modified adsorbent using existing material, which can combat both chemical and biological contaminants from water system.

Several removal techniques including physical, chemical and biological treatment were used to remove such contaminants [3]. However, these techniques are efficient for the removal of either chemical or biological contamination from the water and not effective to remove both. Membrane filtration technology can remove all type of environmental contaminants including chemical and biological pollutants [4]. Membrane filtration including ultrafiltration (UF), microfiltration (MF), nanofiltration (NF) and reverse osmosis (RO), have advantages of high efficiency and easy operation [5]. However, higher rejection rate of membrane filtration technology is still of concern [3]. Therefore, to overcome these issues there is a need to develop a membrane or polymeric matrix, which has high permeability and low rejection rate.

Electrospinning technique is a good alternative to prepare nonwoven nanofibre membranes (NFMs) having comparatively large pore diameter which can reduce rejection rate and increase permeability [6]. Owing to its large pore diameter, electrospun membrane possesses high permeability and found to be suitable for filtering organic contaminants including dyes and other large molecules [7]. However, it is not very effective in removing small sized contaminants like heavy metals and other minute contaminants [8,9]. Thus to tackle both organic and inorganic contaminants there is a need to synthesize membranes which have good permeability and possess excellent adsorptive properties. Though several reports are available to combat inorganic [10], organic [11] or biological contaminant [12] individually, very few reports are based on comprehensive removal of all the afore said contaminants [13,10,14,4]. Adsorption properties of the membrane towards heavy metals could be increased by grafting various functional groups on their surface [10]. Several functional groups

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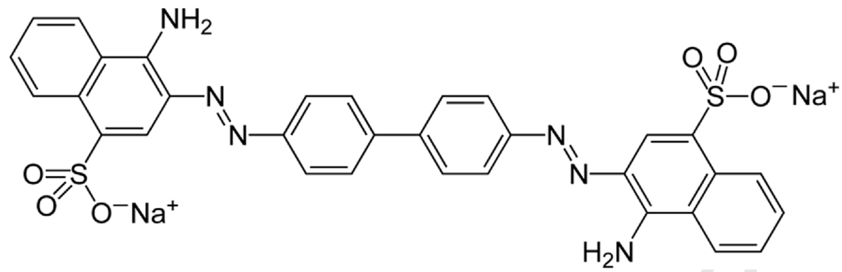


Fig. 1. Molecular structure of Congo Red dye (CR dye).

and ligands like carbonyl, hydroxyl, sulphur and nitrogen containing groups etc., have been found useful to increase the removal efficiency of the polymeric matrix or membrane [15–17]. Among all functional groups, nitrogen based compounds mainly amino, hydrazine, amidoxime and imidazole groups are more effective in forming complexation with metal ions and also enhance the antimicrobial efficiency of the material [18–20]. Polyacrylonitrile (PAN) is widely used for the synthesis of membranes for various environmental remediation applications mainly chemical and biological ones because of good stability, solvent resistance and higher mechanical properties.

Zinc ions are well known antibacterial and antioxidant agent [21]. The Zn ions adhere to the bacterial cells, and penetrate bacterial cellular membrane leading to the cellular disruption, DNA damage, and protien inhibition resulting in death of the bacterial cells [21]. Besides providing bacterial inhibition, zinc ions also find use in the removal of various contaminants including dyes and heavy metal ions.

Thus the present study describes the synthesis of novel amine group funtionalized Zn ion dispersed PAN (Zn/PAN) nanofibers matrix for the removal of chemical and biological contaminants from water. The main novelty of the prepared adsorbent is that it is designed to tackle inorganic, organic and biological contaminants simultaneously. The polymeric matrix in this study is characterized using different analytical techniques such as scanning electron microscopy (SEM), energy dispersive X-rays (EDX), BET Surface analyser, X-rays diffraction analysis, and Fourier transform infrared spectroscopy (FT-IR) and X-ray photo electron spectroscopy. The prepared polymeric matrix was subjected to adsorption analysis for chemical contaminats mainly Cr (VI) ions and CR-dye, and antibacterial activities against *E. coli*, and *S. aureus* bacteria from water.

Experimental

Materials

PAN with an average molecular weight of 150,000 g/mol was obtained from Sigma Aldrich. 98% *N,N*-dimethyl-formamide (DMF), hydrazine sulphate ($N_2H_4 \cdot H_2SO_4$), zinc sulphate ($ZnSO_4 \cdot 7H_2O$), Congo red and 1, 5-Diphenylcarbazide were purchased from Merck India Ltd., India. The reagents like sodium chloride (NaCl), tryptone, agar and yeast extract which are used for the preparation of Luria Bertani (LB) medium, were acquired from hi-media, India. The *E. coli* (K-12), *S. aureus* (RN4220) strains were obtained from different laboratories in India.

Synthesis of Zn dispersed polymeric nanofibers mat

The synthesis of metal-polymer based nanofibers was performed by using electrospinning process. Briefly, PAN (4% w/v) was dissolved in DMF by continuously stirring at 80 °C for 4 h to produce a homogenous solution. Approximately 0.1 g of $ZnSO_4$ was mixed into a homogenous solution of PAN by using continuous stirring at 80 °C for 2 h to produced Zn/PAN based solution. Next, approximately 0.2 g of the hydrazine sulphate salt was added to the Zn/PAN solution. The solution was continuously mixed by using stirring 80 °C for 6 h to form a uniform amine group functionalized Zn/PAN (A/Zn/PAN). The prepared A/Zn/PAN solution was loaded into a 10 mL plastic syringe equipped with a syringe needle, having an inner and outer diameter of 0.3 and 0.35 mm. The solution flow rate in the syringe was controlled by programmable syringe pump (E-spin nano tech, India) to control the solution flow rate. The syringe needle was connected of positive electrode of high voltage supply and a copper plate (dimensions 18 × 18 cm) covered with aluminum foil connected to the negative electrode served as collector. Next, The voltage between the tip of the needle and collector (TCD) was maintained at 10 KV, such that A/Zn/PAN solution stretched/moved towards collector and deposited in the form of A/Zn/PAN nanofibers mat. The tip to collector distance (TCD) and flow rate was kept at 10 cm and 6 mL min^{-1} respectively. The produced A/Zn/PAN nanofibers mat was dried at 80 °C in a vacuum oven for 24 h. Similarly maintaining the same electrospinning conditions, nanofibers mat samples of PAN, Zn/PAN were also prepared for the comparison purpose. The schematic representation of the same is shown in Scheme 1.

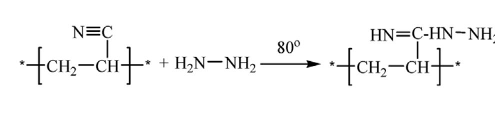
Adsorption analysis

Adsorption experiments for Cr (VI) ions and CR-dye were carried out by batch experiment. For pH optimization experiments initial concentrations of Cr (VI) and CR-dye were maintained at 50 and 10 mg L^{-1} respectively using 50 mg of nanofibers mat in a final volume of 20 mL. The initial pH for Cr(VI) and CR-dye adsorption was varied from 2 to 8 and 4 to 9, respectively and the samples were equilibrated in an orbital shaker at 35 °C. After equilibration, the samples were filtered using 0.22 mm pore size filter paper and the analysis of Cr(VI) and CR-dye was carried out by using UV–vis spectroscopy.

The amount of the Cr(VI) and CR dye adsorbed (mg) per unit mass of A/Zn/PAN mat (g), qe, was obtained by mass balance using the following equation:

$$qe = ((Ci - Ce))/m \times V \quad (1)$$

Where Ci and Ce are initial and equilibrium concentrations of the Cr(VI)metal ion and CR dye (mg L^{-1}), m is dry weight of nanofibers mat (g), and V is the volume of the solution (L). For kinetic studies, the samples were withdrawn at regular intervals



Scheme 1. Mechanism of amine grafting on PAN.

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