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Fabrication of Montmorillonite impregnated cellulose acetate nanofiber membrane and its use for adsorption of Ciprofloxacin

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The paper deals with the fabrication of Montmorillonite impregnated cellulose acetate nanofiber membrane by electrospinning method and the application of the membrane for removal of widely used Ciprofloxacin antibiotic from wastewater. The membrane fabrication conditions were optimized keeping the physical characteristics such as fabrication, strength as basic criteria and its removal efficiency for Ciprofloxacin from wastewater. Very fine nanofiber membranes were formed with an approximate size of less than 100 nm. The adsorption experiments were conducted with initial CIP concentration of 10 mg/L, adsorbent dose of 1 g/L, 3 g/L and 5 g/L at a pH of 4. The contact time was 5 h. The adsorptive removal efficiencies were varying from 27% to more than 90% depending upon the combination used.

Keywords: Ciprofloxacin, cellulose acetate, Montmorillonite, electrospinning, adsorption.

Introduction

Due to increased population there is an increase in evolution of new diseases which needs the production of various pharmaceuticals and antibiotics in the daily use of life. These antibiotics are not completely used up by the body and around 80% to 90% of it is excreted into the environment as a parent compound and hence the amount of antibiotics coming to the sewage plant is directly proportional to the antibiotics being consumed[1,2]. Due to its increase in the day to day life, its concentration is increasing day by day which is getting its pathway to the surface waters and drinking waters. Among other antibiotics present in wastewater, concentration of Ciprofloxacin was measured around more than 31000 μg/L that was found in the effluent wastewater in Hyderabad[3]. Various methods have been studied for the removal of antibiotics from wastewater by using various adsorbing materials or by using UV-H_2O_2 or other advanced oxidation processes[5]. CIP was also removed by MMT[4]. Various adsorbents such as surface modified carbon materials[7], saw dust[8], three dimensional (3D) porous graphene hydrogel[9], long TiO_2 nanotubes/reduced graphene oxide (rGO-TON) hydrogel[10], modified coal fly ash[11], magnetic chitosan grafted graphene oxide composite[12] were used for the removal of CIP from wastewater. Fabrication of Cellulose Acetate (CA) with Montmorillonite (MMT) was also studied for determining the strength of the membrane[13]. In this study, nanofiber membrane (NFM) was fabricated using Cellulose Acetate polymer and impregnating clay Montmorillonite in it for enhancing the removal of Ciprofloxacin (CIP) from wastewater.

Various combinations of Cellulose Acetate and Montmorillonite along with solvent variation have been tried and an optimized combination was chosen for membrane fabrication. Electrospinning was chosen as a mode of fabrication of nanofiber membrane because membranes formed are of large surface to volume ratio with increased porosity which enhances the removal efficiency of antibiotic from wastewater. Further adsorption studies were also carried out to examine the removal of Ciprofloxacin from wastewater.

Materials and methods:

Reagents:

Cellulose Acetate (CA) were purchased from Lobachemicals (CA, Extrapure; acetyl content 45%; MW = 30000 g/mol). The clay, Montmorillionite (MMT) was supplied by Geotechnical Department of IIEST Shibpur. The solvents used were acetone (MW: 58.05), and di-methyl-acetamide in the ratio of 2:1. Along with the above solvents, dichloromethane (DCM) (MW: 84.93), glacial acetic acid (MW: 60.05), N,N-dimethylformamide (DMF) (MW: 73.09), sodium chloride were also used for trial purpose in fabrication process. Ciprofloxacin injection IP (Cifran) (CIP) of concentration 200 mg/100 mL was purchased from Frank Ross, Sakherbazar.

Membrane fabrication:

Electrospinning was chosen as the mode for membrane fabrication of polymer solution. Different combinations were studied by increasing Montmorillonite (MMT) and decreasing Cellulose Acetate (CA) with different solvent ratios and electrospinning parameters. A suitable combination was fixed for Cellulose Acetate and Montmorillonite at a ratio of (5:15) with solvents acetone and dimethyl acetamide at a ratio of (2:1). The whole solution is kept for 2 to 3 days with constant agitation of 1000 rpm for proper bonding between CA and MMT. It was seen that higher strength of the membrane was obtained when the solution was left for more than three days. The solution was fed at a flow rate of 2 ml/min using syringe and electrospun at a positive voltage of 20 KV at a collecting distance of 10 cm.

Analytical procedure:

The Ciprofloxacin concentration was analyzed by double beam UV-Vis spectrophotometer. The scanning was done and wavelength of 263.6 nm was selected to check the adsorption capability.

Results and discussion

Adsorbent preparation:

The clay MMT collected from the laboratory was first ultrasound for 15 min to remove any lump if present. After ultrasound, MMT was washed with distilled water by keeping it in agitation for 24 h which was further filtered and dried in hot air oven at 80ºC for 24 h. After drying, the MMT was crushed to fine powder and kept in storage for further solution preparation. The whole procedure was followed from one of the literature review which fabricated only CA/MMT nanofibre membrane[13]. CA and MMT of different combinations were made by changing solvent variations and electrospinning parameters.

Membrane fabrication:

Different combinations of CA and MMT were taken for trial with different solvent concentration. Electrospinning was selected as the method for membrane fabrication. For electrospinning, ESPIN-NANO, needle based electrospinning machine manufactured by M/s. Peco, Chennai, high voltage power supply – 0 to 40 kV DC was used. Different trials were used for fabrication of nanofibre membrane by electrospinning which are being discussed below.

Preparation of Cellulose Acetate (10%) and Montmorillonite (5%) nanofiber membrane:

Cellulose Acetate (CA) (10%) and Montmorillonite (MMT) (5%) were mixed with acetone and dimethylacetamide at a ratio of 2:1. The flow rate of 2 mL/min and voltage of 20 KV was fixed as electrospinning parameters having the collecting distance of 10 cm. The initial concentration of Ciprofloxacin was taken as 10 mg/L at a pH of 4.00 and at ambient temperature of 28ºC. The above parameters were same for all the combinations. The adsorption of Ciprofloxacin onto nanofiber membrane was examined at different dosages of 1, 3, 5, 7, and 10 g/L where the maximum removal of 85.18% was obtained at 10 g/L for 5 h. The percentage removal of 52.92, 74.59 and 76.62% was obtained for 3, 5 and 7 g/L respectively. The nanofiber membrane formed was of good strength and well fabricated.

Cellulose Acetate (10%) and Montmorillonite (9%) nanofiber membrane:

To increase the percentage removal of CIP, MMT percentage was increased to 9% keeping CA percentage to 10%. The electrospinning parameters and the adsorption parameters were same as the above. The percentage removal of CIP was 87.04% at 10 g/L whereas, the percentage removal of 73.92, 84.75 and 86.70% was obtained for 3, 5 and 7 g/L which was higher compared to the above combination.

Preparation of Cellulose Acetate (2%) and Montmorillonite (9%) nanofiber membrane:

Considering the economic point of view for the nanofiber membrane, lower percentage of CA and higher percentage of MMT was chosen as combination. CA (2%) and MMT (9%) was mixed in the solvents of acetone and dimethyleacetamide at a ratio of 2:1. The electrospinning parameters were kept same as the above combination. The fabrication of the nanofiber membrane was not good and the membrane formed was fragile without any strength. The electrospinning parameters were also changed in order to fabricate the membrane. Due to increase in MMT percentage with a decrease in CA percentage, clotting of needle and inconsistency in electrospinning was obtained. The clay particles could not adhere to the membrane and hence were coming out into the solution which was determined by increase in turbidity of the solution. The turbidity was checked by Nephelometric method in terms of NTU (Nephelometric Turbidity Units). The percentage removal of 87.04% was obtained at 3 g/L adsorbent dosage. Since the membrane formed was not of high strength and good quality resulting in the increase in turbidity of water due to the clay particles, this combination was not used for nanofiber membrane formation.

Preparation of Cellulose Acetate (5%) and Montmorillonite (9%) nanofiber membrane with solvents acetic acid and water (3:1):

For enhancing the membrane fabrication and removal efficiency, CA (5%), MMT (9%) and NaCl (0.1%) was taken as combination in solvents acetic acid and water at a ratio of 3:1. NaCl was used for fabrication because of its leaching effect from the membrane resulting in increased porosity of the membrane which leads to better removal of Ciprofloxacin. The electrospinning parameters were kept same or differed depending on the fabrication of nanofiber membrane. The membrane fabrication was not good and was very brittle without any strength. The percentage removal of 80.86% was obtained at 3 g/L resulting in increase in turbidity of water. Inspite of higher removal of CIP, this combination cannot be used because of its fabrication problem and non adherence of clay particles in the nanofiber membrane. Since this fabrication was not well established, so other combination with different solvents were used for trial.

Preparation of Cellulose Acetate (5%) and Montmorillonite (9%) with solvents acetone and dimethylacetamide (2:1) nanofiber membrane:

CA (5%) and MMT (9%) was taken as combination with solvents acetone and dimethyleacetamide at a ratio of 2:1. The membrane fabrication was same as the above combination without any strength and fragile in nature. The removal of CIP was 52.58% at 3 g/L, 69% at 5 g/L and 74.76% at 7 g/L respectively. Since the fabrication process was not established well, so this combination was also discarded.

Preparation of Cellulose Acetate (5%) and Montmorillonite (12%) nanofiber membrane:

CA (5%) and MMT (12%) was taken as a new combination with the same solvents as above. The fabrication of nanofiber membrane was better than the above combinations. The membrane formed was of high strength without increase in turbidity. The percentage removal of 71.38% was obtained at a dosage of 3 g/L which was higher than the above combination. The percentage removal increased to 78.49% and 81.62% with an increase in dosage of 5 and 7 g/L respectively. Since this combination lead to better removal of CIP, higher percentage of MMT was considered in the next combination.

Preparation of Cellulose Acetate (5%) and Montmorillonite (15%) nanofiber membrane:

CA (5%) and MMT (15%) was chosen as a new combination in the same solvents as above. The fabrication of the nanofiber membrane lead to the formation of high strength membrane with a percentage removal of 68.83% at 3 g/L, 78.23 % at 5 g/L and 84.33% at 7 g/L respectively. The percentage removal was increased to some extent when the time taken for adsorption was 20 h.

Preparation of Cellulose Acetate (6%) and Montmorillonite (15, 17 and 20%) nanofiber membrane:

Since the above combination lead to higher removal of CIP, trial were made with the increase in MMT and CA percentages separately. CA (6%) and MMT (15, 17 and 20%) were taken as combination. All the parameters of adsorption were same as done for the above combinations. The removal percentage of CIP was found to be 88.39, 86.02 and 88.99% at a dosage of 3 g/L, and, 87.72, 90.34 and 90.43% at a dosage of 5 g/L respectively. It is seen that increase in MMT lead to increase in removal efficiency, but also lead to inconsistency in electrospinning and non fabrication of nanofiber membrane. In all the three combinations, nanofiber membrane formed were very brittle without any strength. The brittle nature of the nanofiber membrane can be explained due to the fact that increase in MMT lead to increase in its surface charge thereby hindering the interaction between CA and MMT molecules[13]. The above combinations had an increase in removal efficiency of CIP but failed to maintain the strength of the membrane and fabrication of the membrane. Hence further trial was conducted for fabrication of nanofiber membrane keeping strength and removal efficiency as paramount factors.

Preparation of Cellulose Acetate (7%) and Montmorillonite (20%) nanofiber membrane:

CA (7%) and MMT (20%) was fabricated and removal efficiency was determined. But this combination also lead to non fabrication of membrane with clotting of needle. The membrane formed cannot be peeled out from the ground plate. The removal efficiency was found to be 85.18% for 3 g/L and 91.10% for 7 g/L. The removal percentages were found to be higher as compared to the above membranes but the fabrication was not satisfied to consider it as a membrane. Hence further trials were carried out for fabrication of nanofiber membrane.

Preparation of Cellulose Acetate (7%) and Montmorillonite (17%) nanofiber membrane:

CA (7%) and MMT (17%) was taken as a new combination keeping all the parameters same. The fabrication was much better compared to the other combinations as discussed above. The removal percentage was 91.44% for 3 g/L, 92.54% for 5 g/L and 90.77% for 7 g/L. The membrane formed was fragile and cannot be considered for adsorption process.

Hence it was found from all the above different combinations that CA (5%) and MMT (15%) with solvents acetone and dimethylacetamide at a ratio of 2:1 was considered the best suitable combination with respect to the fabrication, strength and removal efficiency. The electrospinning parameters were fixed at a flow rate of 2 mL/min with a collecting distance of 10 cm and at a positive voltage of 20 KV. The NFM formed after electrospinning is shown in Fig. 1. The percentage removal of CIP was checked in triplicate and hence was chosen for adsorption studies.

Characterization of nanofiber membrane:

Scanning Electron Microscope (SEM) images of NFM were done to characterize the material properties and its constituents. Fig. 2 shows the SEM images of CA/MMT composite fibers with MMT loading of 15%. The surface methodology of CA/MMT nanofibre membrane was characterized by

Fig. 1. Nanofiber membrane of CA and MMT after electrospinning.

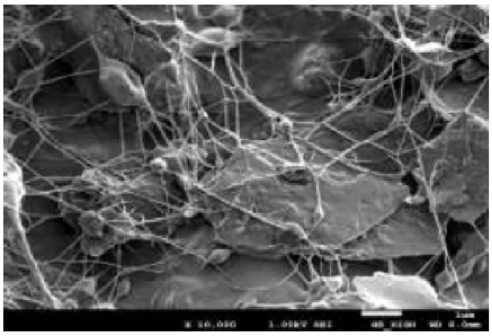

Fig. 2. SEM of nanofiber membrane CA (5%) and MMT (15%).

Field Emission SEM (FESEM, JSM-7610F JEOL) at a magnification range of 1 μm to 100 nm at an accelerating voltage of 1 kV and working distance of 8.00 mm. The specimens were coated with palladium prior to the measurement to prevent surface charging. The composition of the nanofibers its amount shown in Fig. 3 and its amount was confirmed from Energy Dispersive X-Ray Spectroscopy (EDAX, XMAX 50, OXFORD) spectrum and mapping images.

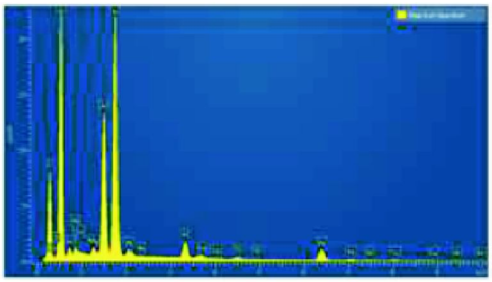

Fig. 3. EDAX analysis of nanofiber membrane CA (5%) and MMT (15%).

Adsorption study:

Adsorption study was conducted with each of the membrane formed and the best fabricated membrane of respective combination was chosen and CIP removal was analyzed. The percentage removal of CIP were done in triplicates and the best trial was reported as shown in Fig. 4 and used for further adsorption studies.

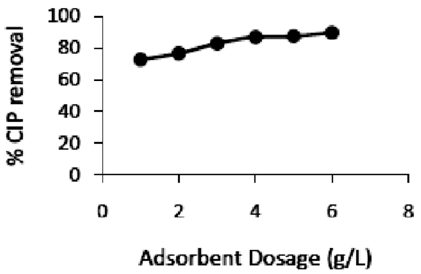

Fig. 4. Effect of adsorbent dosages (nanofiber membrane) on CIP adsorption (CIP – 10 mg/L, pH – 6.00, Temperature – 30°C, shaking speed – 100 rpm, time of shaking = 5 h).

Conclusion

Nanofibre membrane were formed by electrospinning method with the combination of Cellulose Acetate and Montmorillonite at a ratio of (5:15; w/w) with solvents acetone and dimethylacetamide at a ratio of (2:1). Under optimized conditions of membrane fabrication and adsorption study, about 90% Ciprofloxacin can be removed from wastewater. Ciprofloxacin removal by MMT was earlier studied where MMT used was centrifuged and then passed through filter paper of 0.45 μm. CA impregnated with MMT will lead to interaction and bonding between the molecules and hence only normal filter paper is required for filtering the NFM easily when used as an adsorbent without any centrifuging.

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