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Synthesis and Characterization of PMMA Nanofibers for Filtration of Drinking Water

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Abstract

Currently, hundreds of consumer products in cludelarge-scale nanoparticles; this enhances the possibility of such particles to be released into water and in result causesenvironmental and human health issues. In this research, asynthesis of PolyMethylMethAcrylate (PMMA) nano-membrane for the filtration of nanoparticles from natural water is demonstrated. Electrospinning technique is deployed for the synthesis of PMMA nanofibers. The synthesized nanofibers are further optimized by adding Di-Methyl Formamide (DMF) and acetone that provides elasticity and increases the exterior area of the nano-membranes. The resultant membrane is tendbal and instinctivelyrobust enough to resist filtration under high stress. The synthesized nanofibers are further analyzed and characterized by using spectroscopy (UV-Vis), Fourier Transform Infra-Red spectroscopy (FTIR) and Scanning Electron Microscope(SEM).The SEM, UV-vis and FTIR result shows the filtration rate of the fabricated membrane could capably exclude nanoparticles with different sizes (from 10 to 100 nm in diameter) from a feed solution.

Keyword : Electrospinning, Fiber diameter, FTIR, SEM,Water filtration

I. Introduction

Clean and quality drinking water is the current demand of the world especially of the developing and undeveloped countries like Pakistan. Water pollution

was highlighted as quite ecological issues to the humankind concern because of the taint of serious NP execute in wastewater **[**V**].**These particles will endure in natural bodies and donot seem to be completely migrated by potable treatment, thereby mystify a doable public health concern [XXVIII,XXXII]. Therefore, the bud of the latest equipment is required to reduce the potential risks with living things and ecological exposure to nonmaterial [XXIII]. This solicits the researchers to reveal a brand new method within the fields of environmental protection. The water contains significant metals like Cr, Cd,(Hg),and (Zn) with on top of bound limit will cause cancer impact to health of human, hence, many treatments are wont to take away contaminants that embody merger, precipitous, ion exchange, adsorption, filtration, reverse osmosis, biodegradation, membrane separation and solvent extraction [XXXI].Nanofiber webs, because of their massive specific space, terribly tiny pore dimension, and high consistency are exposed to ameliorate the potency of standard materials used for the filtration of distinct materials [XXVIII,VI].

The diameters of polymer fiber are shrunk from (10 nm –100 nm),due to some several superb uniqueness like terribly giant surface area to volume ratio (this ratio is 103 times that of a microfiber), and flexibility in surface and enhanced mechanical performance (e.g. stiffness and tensile potency)which make this different from the other proverbial type of the fabric. Due to these marvelous properties of the chemical compound nano-membrane are useable in numerous vital applications. Several techniques like drawing [XI], template synthesis **[**VIII,XVII], phase separation [XVI], self-assembly [XIV,XXXIII], electrospinning [VII,IX] etc. recently for the preparation of polymer fiber we are using above of all techniques. For a long single nanofibers fabrication in fiber engineering use a drawing method which same as a dry spinning.

Many studies have investigated the electrospinning method [II, X,XXII]. During this analysis work, we tend to square measure the mistreatment electrospinning technique that is a comparatively fast, straightforward and economical way to fabricate nano-fibrous structures [IV]. However, once it involves the results of the method and material each hypothetical and tentativeinvestigationis being regularly conducted [XXIV, XXVII,XXX].This paper aims is to review the results of the PMMA nanofiber water filter by using electrospinning. The PMMA nanofibers selected had a diameter under 1000 nm, which is the thinnest diameter among all preceding studies [XXI,XXV].During this research work, the event of efficient nanofiber membranes for the removals of nanoparticles from completely different nourish solutions is conferred. Agnostic PMMANFwasmade-up by electrospinning from MMA+AIBN precursor solution followed by thermal treatment. Furthermore, DMF and acetone were added to fabricatesuppleness and to extend the explicit surface area of the PMMAnanofibres. The PMMA/DMF+Acetone derived PMMA nanofibres mats were yieldable and showed realistic mechanical potency to

resist filtration under the applied stress. The tentativeconclusionreveals that the membranes may expeditiously eliminate varied NP from various feed water.

II. Literature Review

Research work in [XV] is presented on the basisof Pilot-scale direct filtration challenge experiments were conducted to determine the impact of chemical pretreatment and filter design on the removal of *Cryptosporidium* surrogates dosed into the filter influent water at low temperature. Copolymers-modified microspheres were identified as representative *Cryptosporidium* oocysts surrogates based on our previous findings and were used to evaluate the oocysts filtration removal at this pilot-scale study.In [XXIX],pristine Multi-Walled Carbon NanoTubes (MWCNTs) were functionalized by using Ar/O_2 plasma treatment technique, which enhanced adsorptive membrane filtration of zinc ions from water and wastewater. The XPS analysis showed that plasma treatment largely increased the surface oxygen groups content of MWCNTs from 2.78% to 6.79%.

In [XVIII],River Bank Filtration (RBF) is considered to efficiently remove nitrate and trace Organic Micro Pollutants (OMP) from polluted surface waters. This is essential for maintaining good groundwater quality and providing high quality drinking water. Predicting the fate of OMP during RBF is difficult as the biogeochemical factors controlling the removal efficiency are not fully understood. To determine in-situ removal efficiency and degradation rates of nitrate and OMP indicator substances we conducted a field study in a RBF system during a period of one and a half years incorporating temporally and spatially varying redox conditions and temperature changes typically occurring in temperate climates.

In research [XXXIV],results showed that fiber surfaces of CNC/PMMA appeared smooth. Fibers had gradually decreasing diameters and lower diameter variations as CNC loading increased. The thermal property of CNC/PMMA nanofibers was also enhanced due to hydrogen bonding between PMMA molecular chains and CNC nanoparticles. Compared to pure PMMA fibers, the storage modulus and tensile strength of composite nanofibers were pronouncedly improved.Their findings provided useful guidelines for the fabrication of nanofibers with desired properties and pore structure by electrospinning.

Research work in [XX]showed the fabrication of nano fiber for water filtration application b using of electrospinning technique. Different polymers such as polyacryolonitrile, polyamide, polyethylene terephthalate, polyvinylidene fluoride, polyvinyl alcohol, polysulfone, polyethersulfone, nylon-6, poly(ethylene oxide), polystyrene, cellulose acetate, and many more have been used to prepare nanofiber membranes. To enhance their performance, various nanomaterials such as carbon nanotubes, titanium dioxide, zinc oxide, iron oxide, silicon dioxide, nano-clays,

cylcodextrins, etc., have been embedded or coated on the surface of nanofiber membranes.

III. Research Methodology

A. Materials and Method

Poly (methylmethacrylate)(PMMA) (Mw=120,000g/mol) was selected as the polymer for potential future research and applications, N-N dimethylformamide (DMF) (20-50) %, and Acetone (80-50) % were purchased from Sigma-Aldrich. Methyl methacrylate (MMA) use is a monomer and 2, 2'-azobisisobutyronitrile (AIBN) initiator.

B. Preparation of PMMA nanofibrous membrane

Heat Initiated Polymerization (HIP) MMA is frequently initiated by thermally labile compounds such a 2.2'-azobisisobutyronitrile (AIBN). Heat initiatedpolymerization method we are using for the PMMA nanofiber solutionfor the advance-guard solutions of PMMAnanofibres at concentrations range from (5 to 10)wt% in DMF+Acetone at (60-70) C^0. PMMANF solutions was prepared by the accumulation of ACETONE and DMF to the PMMA solution to accomplish the proper PMMA/DMF+Acetone; the dataof which is given in Table 1**.** Polymer solutions were mixed by a magnetic stirrer until they become harmonized. The viscosity and electrical conductivity of the polymer solution were measured by a digital viscometer (DV-E, Brookfield Co) and an electric conductivity meter (CRISON EC-meter BASIC) at $25C^0$. The resulting harmonized solution was degassed for 15 minutes to get the bubble free clear solution. Collections of the NF membrane on aluminum foil which as a like collector,synthesized by electrospinning. The Electrospinning flow rate of homogenous PMMA is 3 ml/h with a high voltage of 20 kV at room temperature. The distance between the syringe tip and collector plate is variable (6-8) cm.

C. Groundwork of the NP Solutions

The filtration efficiency of PMMANFS was appraised with different types of NP mixture (i.e. Drain water blue water and rainwater). The concentrations of the NP solutions were attuned to have a high ultraviolet-visible (UV-Vis) absorbance without signal infiltration.

D. Characterizations of PMMA nanomembrane

The morphology of the nanomembranewasdeliberate by the help of a scanning electron microscope (SEM). Analyzedthe PMMANF thickness (diameter) with the help of ImageJ software and at least four pictures were used to calculate the

average values of the fibersdiameter. A Fourier transform infrared (FTIR) spectrum of the sample was recorded on the α-Brucker model using PMMA solution in the range of 400–4000 cm^{-1}.The pore size of PMMANF membranes were investigatedby using a simple particle removal method. Feed water solution contains a particle with a diameter between 0.1 μm and 3 μm were passed through the membrane at the pressure of about 0.1 bar. The absorbance of the nourish and filtrate latex solutions was deliberateb using a UV-visspectrometer.

IV. Results and Discussion

A. Synthesis and Characterization

PMMA In this study, polymethyl methacrylate (PMMA) was repaired by heat initiated polymerization (HIP) in an organic solvent as white solid Figure 1.In this polymerization process, the first step that takes place is the reaction between methyl methacrylate (MMA) monomer (10 g, 100 mmol) and 2, 2'-azobisisobutyronitrile (AIBN) (0.1 g, 0.41 mmol) which acts as an initiator. The activated AIBN can be combined with the MMA monomer. In the process of transferring the unpaired electrons to the monomer unit, the initiator will be activated. The polymer MMA can continue growing with the active part shifted towards the end chain. The solution was heated to 70 Cº [III,XIII]. The solution was stirred to form a harmonized solution, ensuring that the reaction proceeded to the conclusion. In this study, the polymerization time was 30 minutes.

Figure 3 shows that thin the independent absorption band between 1140 cm^{-1} to 1240 cm^{-1} in each infrared spectrum of MMA andPMMA, that manifestation to [–C-O-C-] stretching vibration. The band wavelength 1735 cm^{-1} within the MMA spectrum and 1724.14 cm^{-1} in the PMMA spectra confirms the presence of C=O of ester. The two bands appeared between 3000 cm^{-1} and 2900 cm^{-1} in each spectrum attributed –CH sp^3band. It can be observed that the absorption band of -CH sp^3 in MMA was weaker compared to PMMA due to there was only one –CH sp^3 bond present in MMA before polymerization. The disappearance of these two functional groups suggested that MMA was successfully polymerized to PMMA by heat initiated polymerization (HIP).

MMA MONOMER

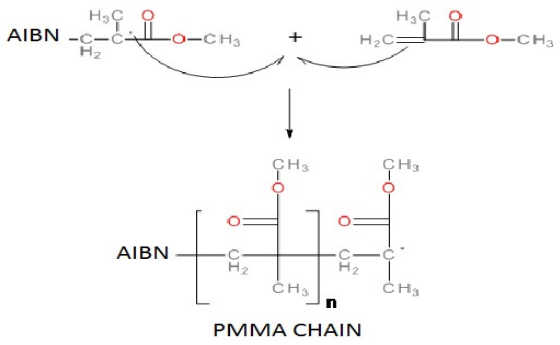


Fig1: White acrylics glass of synthesized PMMAFig2: Heat initiated polymerization
Chain of PMMA.

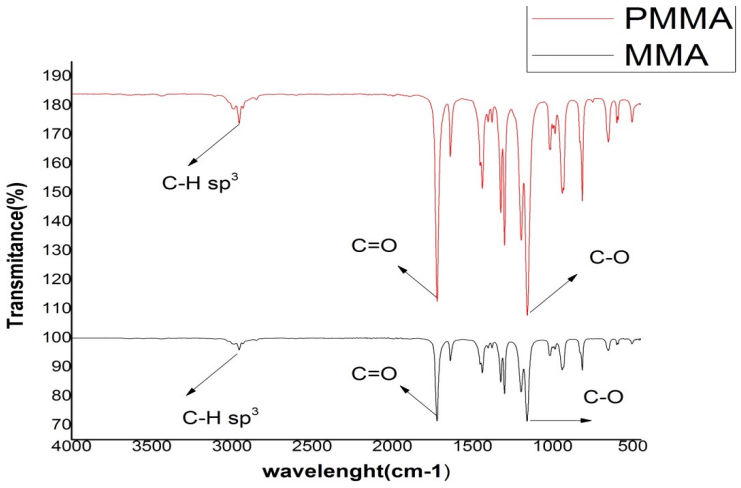


Fig3: FTIR spectra of PMMA and MMA

A. Electrospinning of PMMA nanofiber

Electrospun fibers morphology depends on different conditions**,** to which we control the resultant fibers diameter range from 20 nm to a few micrometers. Morphology and diameter of the electrospun fiber are discussed which changes with conditions. The Dielectric constant of PMMA is in the range 3 to 4 depending on its molecular weight. All substance (solvent) can dissolve in PMMA due to the high dielectric constant. According to Sun.Z and et al, the solvent having a high dielectric constant is better for the electrospinning process due to the electrostatic energy that requires ionizinga solute of the polymer suspension. The most of polymer dissolved in a substance (solvent) with a low dielectric constant.

Effect of PMMA concentrations

The PMMANF properties, depending on the stickiness (viscosity) of polymer solution concentration (cluster). The more complicated polymer chain is the result of high precursor concentration, whichfabricates wide-ranging fibers. The concentration of PMMA in this study varies from (5 to 10) wt% in DMF/Acetone mixture. Gradually**,** increase the diameter of the average fibersof PMMANF with increasing polymer concentration (i.e. 500 nm at 5 wt% to 1000 nm at 10 wt %).Hence viciousness is affected by NF diameter. At higher viscosity there are supplementary chain entanglements and less chain mobility, leading to less extension throughout spinning, so mechanized thicker fibers. As shown in Table 1, for each resolution, a special operational condition was set to provide nanomembrane in an exceedingly through nonstop and stable electrospinning method. The common fiber diameter was resolute from the ImageJ software system. It is seen from table 1 that the fiber diameter (thickness) inflated with a rise polymer solution concentration and contrariwise. Figures 4 and 5 show the SEM result of PMMAnanofibres.

Applied voltage and spinning distance

PMMANF diameter are affected with the applied voltage and if we increase the voltage so in result the diameter of fiber will go to decrease and vice versa. Thedistance between the tip of the syringe and Aluminum plate (collector) is directly related to the morphology of NF. If this distance is smaller than 10 cm, so the polymer solution doesnot have enough time to vary into a fiber form due to the presence of the high-voltage fields. On the other side, if the tip-to-collectordistance is just too enormous (e.g. over 20 cm), the created fibers cannot fly properly toward the collector. In alternative words, in an exceedingly vary from(6 –20) cm, the chemical compound solution has enough traveling time (from needle to the collector). The

prompt vary for the distance ratio was supported by the suggestion within the literature[XIX].

Table 1:Electrospinning parameter on the resultant morphology of the PMMA nanofiber

S.No	PMMA Wt%	Acetone (ml)	DMF (ml)	Voltage Kv	Collection distance cm	Gauge	PMMA nanofiber Diameter (nm)	Morphology
01	05	06	Without DMF	20	08	21		Beaded-fiber
02	05	06	02	20	06	19	500±30 nm	Nanofiber
03	10	04	02	20	07	21	1000±15nm	Nanofiber

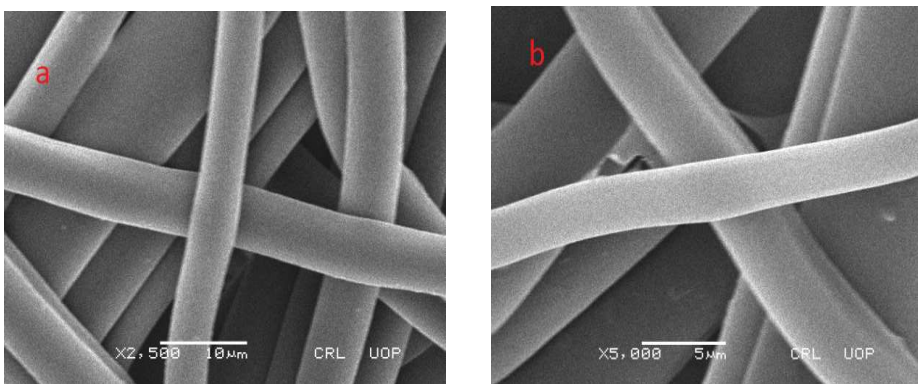


Fig4: SEM images of PMMANF and concentration ratio is (5wt %).

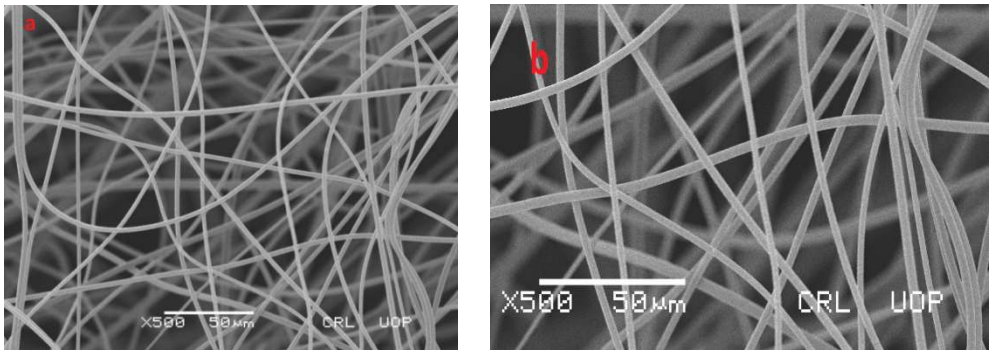
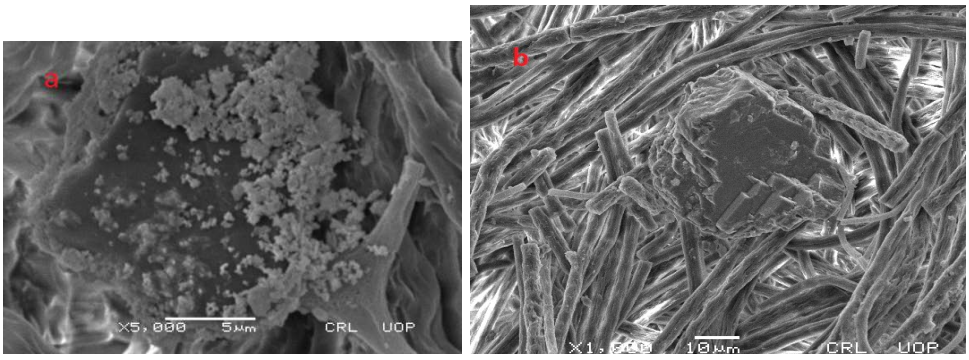


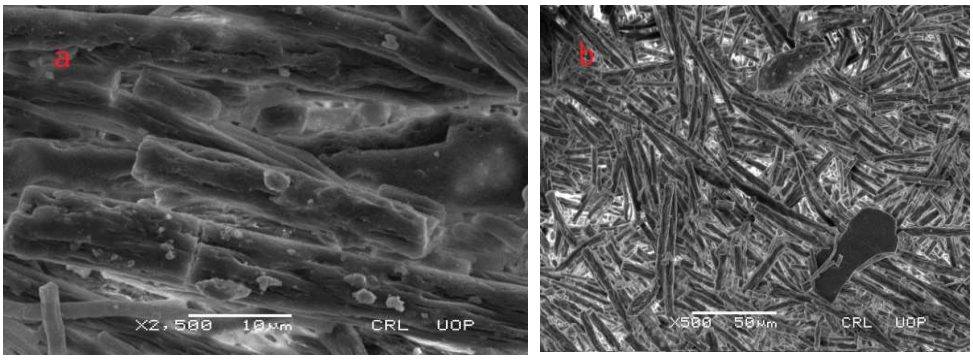
Fig5: SEM images of PMMANF and concentration ratio is (10 wt %).

Water Flux and fiber size

PMMAnanofibresare exposed to supply significant will increase infiltration potency at a comparatively little reduction in porosity [I]. Moreover, in several laboratory tests and actual operational environments, NF filter media have additionally enabled new levels of filtration performance and extend thecapability to retain pollution compared to traditional fibers because of their unique structure. Many fields are used for the uniform and smooth NFs [XII].Every one of them contains a completely diversemenstruationhypothesis and it's typically seen that dissimilar results by menstruation of indistinguishable membrane victimization anddiverse strategies. Filtration of binary compound NP Dispersions Recently, Lin et al**.** **[**XIX] according to the investigation of an automatically sturdy and thermally tolerant nano-membrane via electrospinning of Nomex resolution. Thepreparation of membranes within the sort of nanofibers dramatically increased the particular expanse of the membranes compared to the industrial Nomex fibers. Besides, their nano-fibrousincontestable an extremely economical rejection of NP from a solution. This observation considerably tried the high probable of chemical compound nano-membrane for filtration because of their large chain (polymer). Here, the membranes made by the PMMA of electrospunfrom polymer solution were at start wont to evaluate the purification ability of PMMAnanofibres. The efficiency of the PMMAnanofibres was evaluatedwith the help of different types of NPs, together with an NP kind completely different feed water solution i.e. (blue water, rain and drain water). For its analysis, we tend to use SEM analysis, UV-Vis and FTIR analysis; the resultsare given in figures 6 and 7.



(a)



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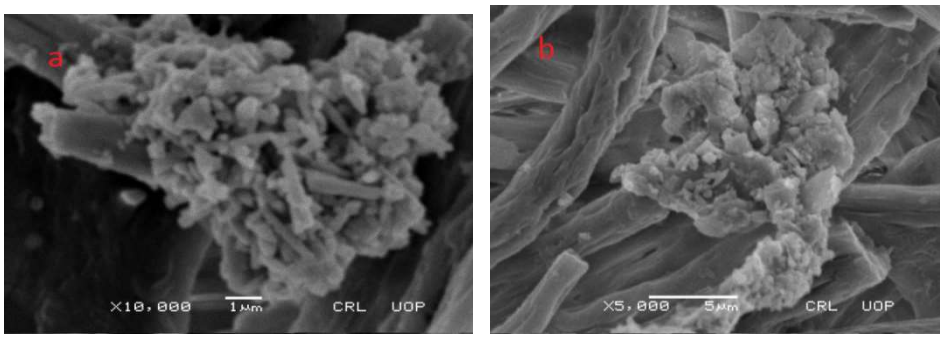
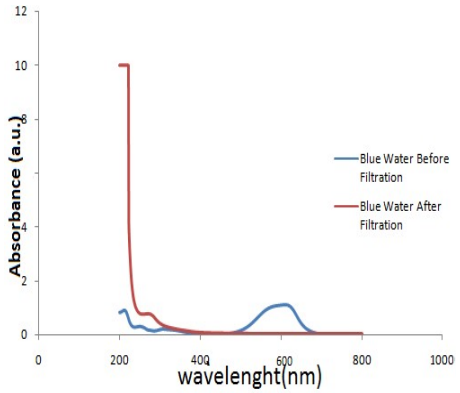
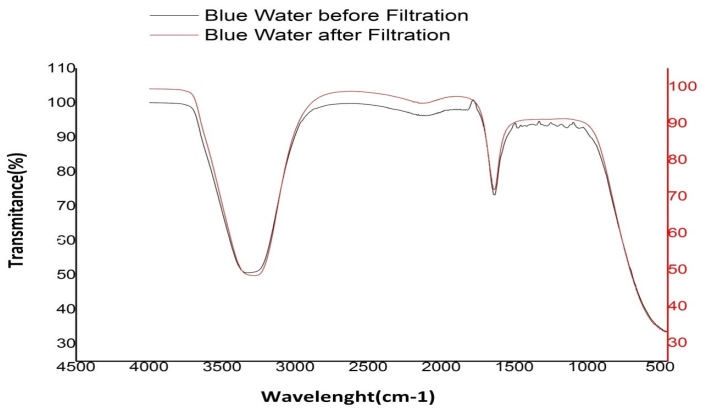


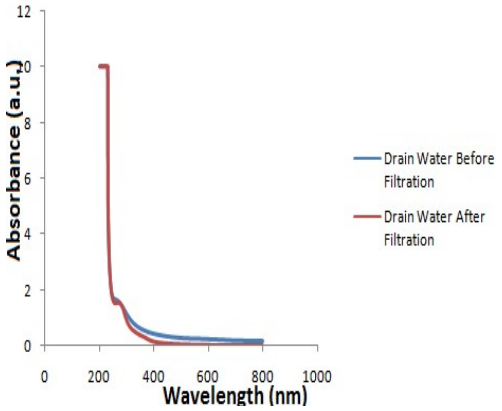
(c)

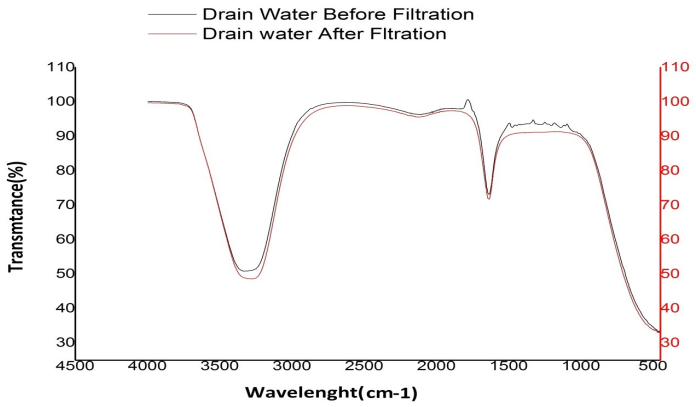
Fig 6: PMMANF membrane top surface SEM result after filtration of blue water with (a) Beads surface (b)Drain water (c)Rain water.





(a)





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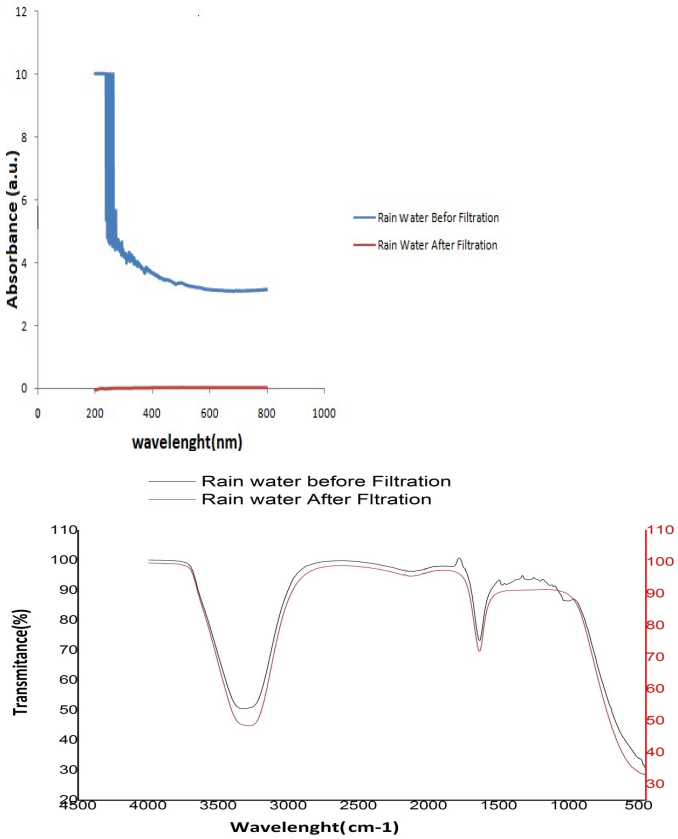

(c)

Fig7: Comparisons of FTIR and UV-Vis spectra's of feed and filtrate water showing the filtration efficiency PMMANP filter in case (Blue NP (a) , Drain NP (b) and Rain NP (c))

For the dispersions of NP**,** we use an intense colure. The efficiency of the filter in time of drain water was determined by UV-vis spectrum as result shown in Figure 7**,** which shows a function of NP size. The nanostructure PMMA filters were able to maintain about 95% of the bluewater NP of 100, 50, and 25 nm. However,the efficiency dropped about 65% in case of blue water due to small size of NP. The filtration rate is highest in the case of rainwater, and at a Small scale, large NP are visible on the surface of single nanofibers. The SEM image is evidence that the minute size of the nanofiber filter. The result of SEM analysis shows the efficiency of PMMA nanofiber in figure 6(a, b and c) and figure 7(a, b andc) [XIX].

V. Conclusion

The aim of this research work is that to demonstratemembranes for the filtration of NP from water which have a high efficiency of filtration, tunable pore size, very high permeability and low cost-efficient way by electrospinning. Clean and quality drinking water is the current demand of the world especially of the developing and undeveloped countries like Pakistan. Available water filters in the local market like Reverse Osmosis (RO) and Microfilters are expensive, bulky (Not potable), require electricity to operate and in-efficient like nanofilters. Hence this research work is carried out to engineer a nanofilter which is cost-effective, does not require electricity to operate potable and rapid (filtration rate of the proposed filter is 0.2 liter/minute at 1 cm^2Aria). This filtrate is useful even to filter the rain and sewerage water from salts, heavy metals and germs and make it suitable for drinking. Recently, it was reported in the news that several people die each year in Pakistan because of drinking unsafe water. The designed nanofilter is also useful to be used in remote places of Pakistan like Baluchistan and Sind and similarly in African countries where people drink rain and sewerage water.

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