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Potential of nanoparticles for water purification: a case-study on anti-biofouling behaviour of metal based polymeric nanocomposite membrane

Soumitra Kar[a,*], M. Subramanian[b], A.K. Ghosh[a], R.C. Bindal[a], S. Prabhakar[a], J. Nuwad[c], C.G.S. Pillai[c], S. Chattopadhyay[b], P.K. Tewari[a]

[a]*Desalination Division, Bhabha Atomic Research Centre, Mumbai – 400085, India*
Tel. +91 22 2259 5602; email: soubiswa@barc.gov.in
[b]*Bioorganic Division, Bhabha Atomic Research Centre, Mumbai – 400085, India*
[c]*Chemistry Division Bhabha Atomic Research Centre, Mumbai – 400085, India*

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ABSTRACT

Nanotechnology is a potential augmentation to the existing water purification technologies. Four different types of functional nanomaterials, like carbon nanotubes, metal/metal oxide nanoparticles, dendrimers and zeolites, are currently under evaluation for water purification application. Nanomaterials offer excellent opportunities because of high surface area (surface/volume ratio), but the challenge is to build up an integrated scalable system. Membranes, because of being energy-economic and having the ability to get associated to different processes as a pretreatment or post-treatment stage, find tremendous applications in the field of water purification. Nanostructured materials serve as a wonderful tool towards development of high flux, high selective membranes. Here attempts are made to develop biofouling resistant membrane. Nanoparticles of silver, copper and silver–copper mixture were impregnated on to the polysulfone host matrix and the biofouling resistance behavior of each membrane surface was examined. The performance of the membranes was evaluated in terms of pure water permeability and solute rejection studies. The membranes were characterized using scanning electron microscopy, energy dispersive X-ray, water contact angle and atomic force microscopy studies. The authors conclude that the silver impregnated membranes possess the best biofouling resistant behavior. The present paper discusses the potential of nanoparticles for water purification and explains briefly the R&D work carried out in the research centre towards development of a biofouling resistant nanocomposite membrane.

Keywords: Nanoparticles; Water purification; Nanocomposite membrane; Biofouling

1. Introduction

Water, the prime cause of life on the Earth, is going to be a cause for violent conflict amongst different states sharing international river basins. The fresh water resource, though already scanty, is becoming increasing scarce because of rapid population growth, hectic urbanization and highly injudicious use. The present scenario calls for the upgrade of existing water purification technologies to augment and cater to the need of humanity. This necessitates to look into nano-enabled technologies which have shown promising potential in the field of water purification and wastewater treatment.

Four classes of nanoscale materials that are being evaluated as functional materials for water purification: (a) metal-containing nanoparticles, (b) zeolites, (c) carbonaceous nanomaterials and (d) dendrimers. The said materials are important with respect to water purification applications because of having high surface area and

*Corresponding author.

many high-energy disordered/defect sites suitable for contaminants uptake. Moreover, the particles can be desirably functionalized for specific uptake of contaminants.

Metal and metal oxide nanoparticles were reported to absorb large amounts of halogen molecules up to 20% by weight, and their efficient anti-bactericidal activity was assessed by different group of researchers [1–6].

Zeolites have been evaluated as ion exchange media for the removal of heavy metals from acid mine wastewaters. The use of synthetic NaP1($Na_6Al_6Si_{10}O_{32}\cdot 12H_2O$) zeolites was reported to remove Cr(III), Ni(II), Zn(II), Cu(II) and Cd(II) from metal electroplating wastewater [7]. Zeolites were reported to result in high flux reverse osmosis nanocomposite membrane without compromise in selectivity [8].

Carbon nanotubes (CNTs) were reported [9–12] to have been used for removal of lead, cadmium, fluoride, and arsenate contaminations from water. It was observed that alignment and functionalization of CNTs are important in deciding the sorprtion capacity of CNTs. A well-controlled defined macro architecture of aligned CNTs was reported for removal of petroleum products and microorganisms [13]. The importance of bringing about an integrated system of CNTs was also emphasized by the researchers [14].

Dendrimers are symmetrical and spherical macromolecules, comprising a relatively dense shell composed of a core, branching sites and terminal groups that usually form a well-defined surface. Their interior may be similar or very different from the surface of the molecule. Chemical and/or physical properties, such as reactivity, complex or salt formation, hydrophilicity and so forth can be varied and optimized to find its applicability in water purification and wastewater treatment [15–20].

The authors believe that the properties of nanomaterials can be truly exploited in impregnating them on the membrane surface rather than using as-grown nanomaterials. The use of nanomaterials without a host matrix may increase the risk of leaching out of nanomaterials into product water making the water unsafe for usage. A lot of work on the development and application of nanocomposite membranes for water purification and wastewater treatment have been carried out recently [21–26]. The comprehensive review on use of nanoparticles in polymeric and ceramic membrane structures with emphasis on manufacturing procedures and performance improvement for water treatment was given by Kim and Bruggen [27].

Desalination Division of Bhabha Atomic Research Centre has been extensively associated on development and application of processes/products for water purification. The R&D work has led to the development of commercially viable polymeric membrane assisted fluoride, arsenic, iron and microorganism decontamination technologies both for domestic as well as community purposes. The present work is focused on development of nanoparticle embedded membrane with better biofouling resistant behavior which will be used in wastewater treatment. The authors initiated the present studies with an intention to see if the bactericidal properties of silver nanoparticles can alter in presence of nanoparticles of copper. Nanocomposite polysulfone (PS) membranes with incorporation of nanoparticles of silver (Ag), copper (Cu) and silver–copper mixture (Ag + Cu) were synthesized and characterized using scanning electron microscope (SEM), energy dispersive X-ray (EDX) and contact angle goniometer studies. The anti-biofouling behavior of the membranes was analyzed.

2. Experimental

2.1. Membrane preparation

Aldrich nanopowders of silver, copper and silver–copper mixture (98% Ag; 2.5% Cu) with particle size &lt100 nm were used for experiments. Four different dope solutions were prepared using polysulfone (M/S Solvay), *N*-methyl pyrrolidone (NMP) (M/S Sisco Research Laboratories, India) and nanoparticles. The composition of the dope is shown in Table 1. A homogeneous dope solution was obtained using ultrasonicator. The membranes were prepared using immersion precipitation technique under a relative humidity of 40% using demineralized water as gelling medium at 25 °C without use of any additives. The thickness of all the membranes was controlled using Doctor's knife with a gap of 200–250 μm.

2.2. Membrane characterization

The water permeability of all the membranes was determined using cross-flow filtration unit at 2 bar pressure. Neutral uncharged solute of polyethylene glycol (PEG, Fluka) and polyethylene oxide (PEO, Fluka) of different molecular weights were used to determine the average pore size of the membranes. The concentration of PEG/PEO was taken 200 ppm in the feed. The exact concentration in the feed and permeate was calculated

Table 1
Composition of dope solutions prepared

Membrane	PS(g)	NMP (g)	Nanoparticle(g)
PS	18	82	NIL
PS + Ag	14.8	82	3.2 (silver)
PS + Cu	14.8	82	3.2 (copper)
PS + Ag + Cu	14.8	82	3.2 (silver–copper)

using TOC analyzer (Thermo Electron Corporation, Model No. TOC1200).

The pore size, shape and surface morphology of the polysulfone membrane and PS nanocomposites were characterized using SEM (Model: SERON AIS2100, South Korea). Each membrane having an area of 0.5 cm^2 was cut and coated with 25 nm of gold using sputter coater in order to make membrane electrically conducive for SEM imaging to reduce the effect of charging. All the micrographs were recorded at same magnification (×10K) and scale (5 μm) for better comparison purpose. The elemental analyses of the membranes were performed using EDX (Model: OXFORD INCA E350, UK). Correction for conductive gold coating was not given during the data acquisition, so gold peaks are invariably present in all the shown spectra. Water contact angle image sequence was taken through a CCD camera of goniometer from GBX instruments, France. Average roughness of the membrane surfaces was measured using NTMDT (Solver) atomic force microscope (AFM).

2.3. Bio-fouling studies

Syto stain was purchased from Invitrogen, Carlsbad, USA. Tryptone, yeast extract and agar were from Difco Laboratories, Detroit, MI, USA. Sodium chloride was procured from Thomas Baker (Chemicals) Limited, India.

Overnight culture of *E. coli* strain MD 1655 was used for fresh inoculation. The culture was grown to mid-late lograthmic phase (~10^8 cfu/ml) in sterile Luria broth upon incubation at 37 ºC under shaking conditions (150 rpm). The bacterial culture thus obtained was used to test the different membranes for viability and adherence studies.

The bacterial culture was used as the feed flow in the membrane assembly mounted with the different test membranes. After 2 h of flow the membrane coupons were retrieved from the assembly and rinsed twice with sterile saline. Circular cross sections (4 mm) were punched out from different regions on the membrane and tested for bacterial viability and adherence.

Representative cross-sections obtained as above were subject to microscopy studies to analyze the extent of adherence of bacteria to each of the membrane. For this purpose, the membrane sections were stained with nuclear stain SYTO (6.7 μM final concentration) for 15 min in dark. The membrane sections were rinsed in saline twice and observed under carlzeiss Axioplus fluorescent microscope with blue excitation (488 nm). The adhered bacterial cells glow green due to SYTO binding to DNA. For every sample membrane at least four different cross-sections were observed under the microscope. For each cross-section 10 fields were observed. Representative images were acquired with microscope associated camera and software.

For viability studies, the cross sections from each test membrane were placed on Luria agar plates with a sterile forceps. The plates were incubated at 37 ºC for 24 h. At the end of incubation the presence or absence of growth was observed visually and the images were obtained by scanning the plates.

3. Results and discussion

3.1. Membrane performance studies

Pure water permeability and solute (PEO: 200 kDa) rejection data of all the membranes are given in Table 2. As evident from the data in Table 2, the water permeability was found to be more in all the nanocomposite membranes compared to pure polysulfone membrane. The water permeability is maximum in copper embedded membranes due to leaching out of copper into gelling medium, which in turn was also verified from EDX studies shown in the next section. From solute rejection studies the characteristic pore radius was found close to 20 nm based on correlation reported by Howe and Clark [28].

3.2. SEM–EDX studies

The microstructure of polysulfone and nanoparticle embedded membrane surfaces are shown in Figs. 1–4.

Table 2
Performance analysis of membrane samples

Membrane	Pure water permeability (LMH)	% Solute rejection
PS	24	95
PS + Ag	28	94
PS + Cu	39.5	90
PS + Ag + Cu	34.3	92

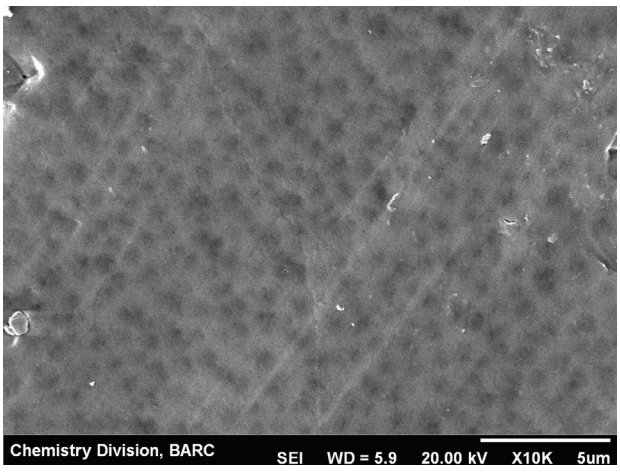

Fig. 1. SEM micrograph of polysulfone membrane surface.

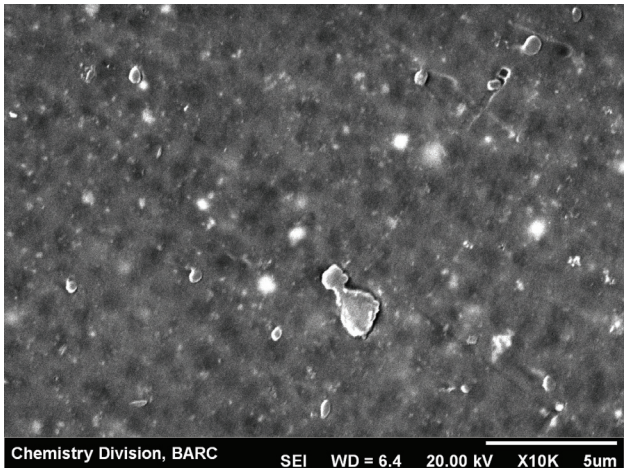

Fig. 2. SEM micrograph of polysulfone–silver membrane surface.

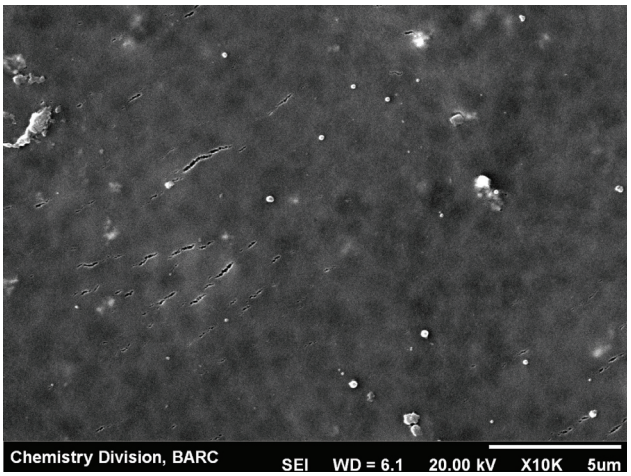

Fig. 3. SEM micrograph of polysulfone–copper membrane surface.

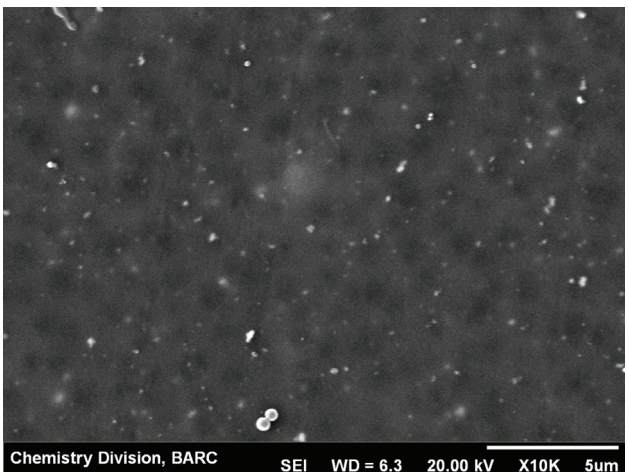

Fig. 4. SEM micrograph of polysulfone–silver–copper membrane surface.

The pores of all the membrane samples ranged from ~10 nm up to ~100 nm in diameter. However, more number of pores was found to be around 80 nm size based on the examination of membrane coupons with SEM at different locations without use of any statistical method. These membranes are typically ultrafiltration (UF) type. Figs. 2–4 clearly show the impregnation of nanoparticles on to polysulfone base membrane. It is clear from the SEM micrographs that the nanoparticles are monodispersed on the host the matrix, whereas, at very few locations the small aggregates are observed.

Elemental analyses of the membrane surfaces were carried out using EDX to ascertain that other than the desired elements no other elemental impurities are present, which helped in correlating the observed antibiofouling performance with the element present on the membrane surface. In the EDX spectra (Fig. 5) of polysulfone membrane, only carbon, sulphur and oxygen peaks were obtained, whereas respective elemental peaks were obtained along with C, S and O peaks in the concerned nanocomposites (Fig. 6–8). Gold peaks were found invariably in all the membrane samples because gold correction was not applied. The density of copper nanoparticles was observed to be less as shown in Fig. 3. This is because of leaching out of copper nanoparticles

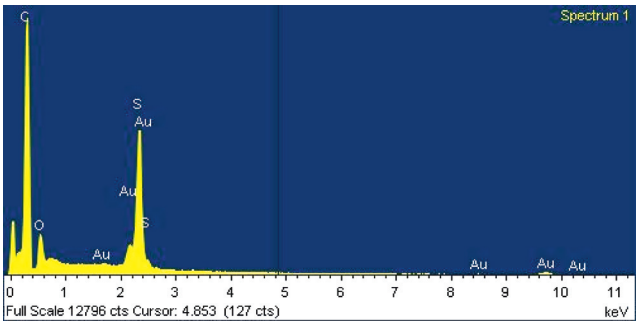

Fig. 5. EDX spectra of polysulfone membrane surface.

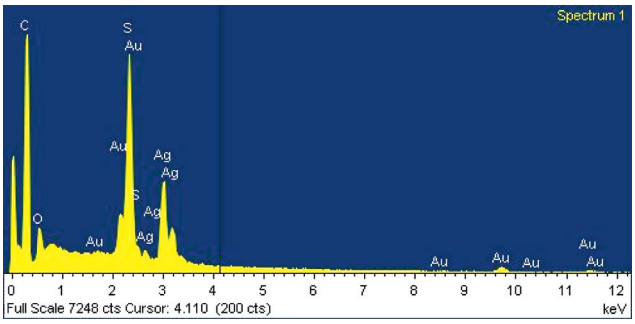

Fig. 6. EDX spectra of polysulfone–silver membrane surface.

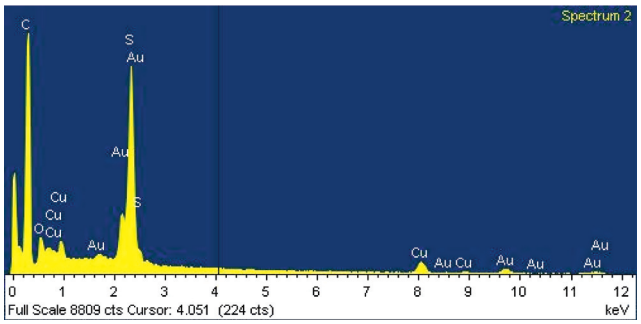

Fig. 7. EDX spectra of polysulfone–copper membrane surface.

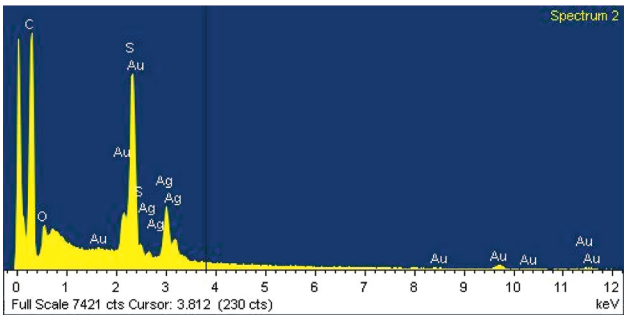

Fig. 8. EDX spectra of polysulfone–silver–copper membrane surface.

into the gelling medium (water) during membrane synthesis step. This is confirmed from the EDX data as shown in Fig. 7 where the intensity of copper peak is very low. The copper peaks were not at all observed when a mixture of silver and copper was incorporated into polysulfone matrix as shown in Fig. 8, which signifies that the tendency of copper to leach out is more in presence of silver in the matrix.

3.3. Contact angle studies

The profile of water contact angle on each of the membrane surface as a function of time is given in Fig. 9. The base polysulfone membrane has water contact value around 71°, whereas for silver based nanocomposite membrane it looks to be little bit more hydrophobic with water contact value of around 72.5°. On the other hand, copper embedded polysulfone membrane (contact angle value: 69.8°) was found relatively more hydrophilic compared to pure polysulfone membrane. Moreover, the membrane with both copper and silver showed a behavior close to polysulfone membrane. The extent of hydrophilicity and hydrophobicity can be changed depending upon the amount of nanoparticle loading.

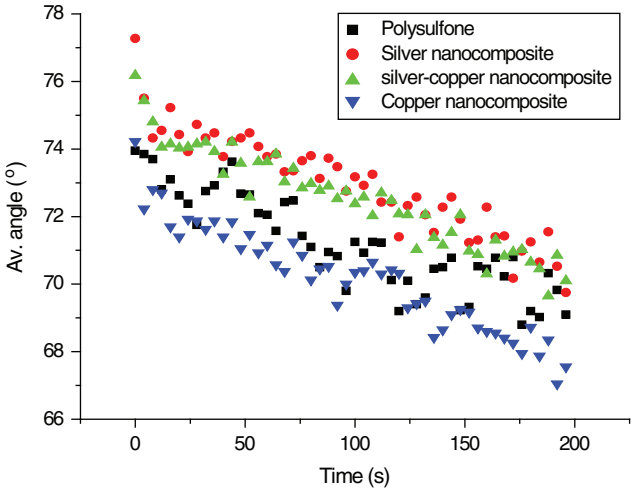

Fig. 9. Contact angle measurement studies on polysulfone and nanocomposite membranes.

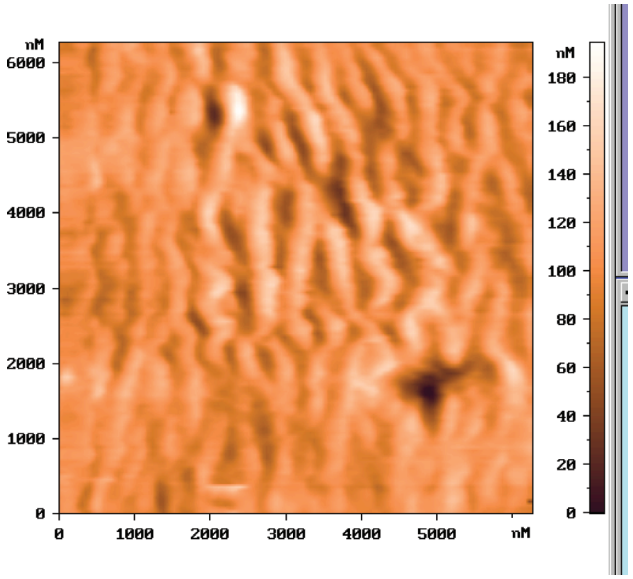

Fig. 10. AFM 2D picture of polysulfone membrane surface.

3.4. Membrane surface roughness studies

Atomic force microscopic 2D views of all membrane surfaces are shown in Figs. 10–13. The average surface roughness of pure polysulfone membrane was found to be around 16.4 nm. The surface roughness was found to increase with incorporation of nanoparticles. The values of average surface roughness for silver, copper and silver–copper mixture embedded polysulfone membrane were found to be about 23.8 nm, 27.0 nm and 37.4 nm, respectively. Similar trend was reported in the literature for PVA/clay nanocomposite membrane [29].

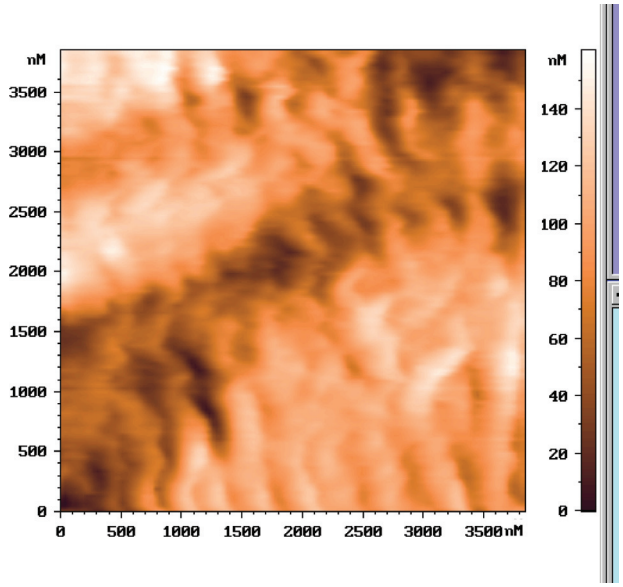

Fig. 11. AFM 2D picture of polysulfone–silver membrane surface.

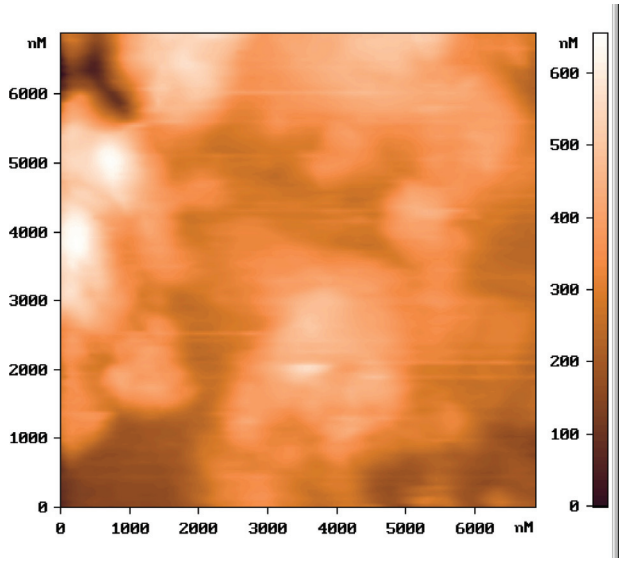

Fig. 12. AFM 2D picture of polysulfone–copper membrane surface.

3.5. Studies on bio-fouling resistant behavior of membrane surface

The membrane sections, after being flushed through feed containing bacteria culture, were stained with nuclear stain SYTO (6.7 μM final concentration) for 15 min in dark. The sections were rinsed in saline twice and observed under carlzeiss Axioplus fluorescent microscope with blue excitation (488 nm). The adhered bacterial cells glow green due to SYTO binding to DNA.

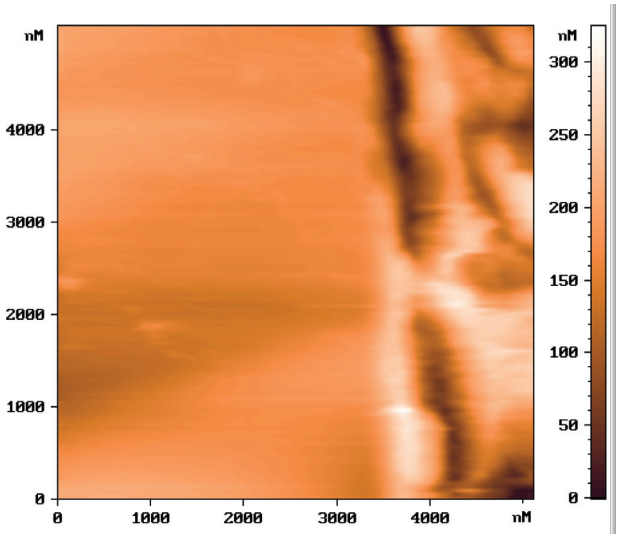

Fig. 13. AFM 2D picture of polysulfone–silver–copper membrane surface.

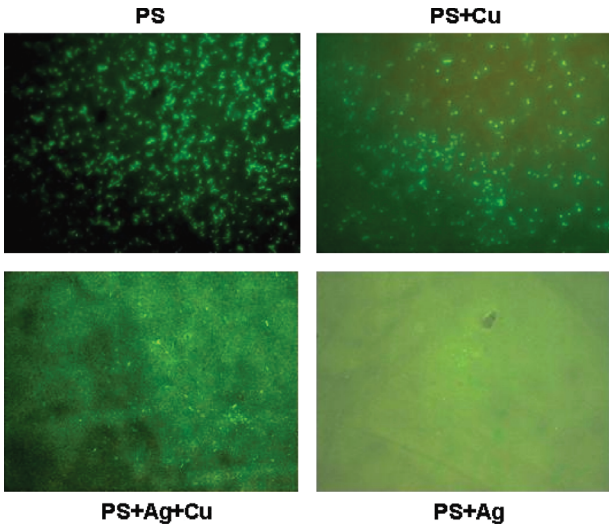

Fig. 14. Bacterial adherence studies on membrane surfaces.

From the results shown in Fig. 14, it is evident there is decrease in adherence of bacteria on the nanocomposite membranes compared to the pure polysulfone membrane. The adherence is minimum in case of silver impregnated membrane.

Representative cross-sections were punched from each membrane after they are flushed with bacteria culture, and placed on Luria agar plates and incubated at 37 °C overnight. The results (Fig. 15) showed growth of bacteria in PS and PS + Cu while no bacterial growth was detected in PS + Ag and PS + Ag + Cu. This confirmed

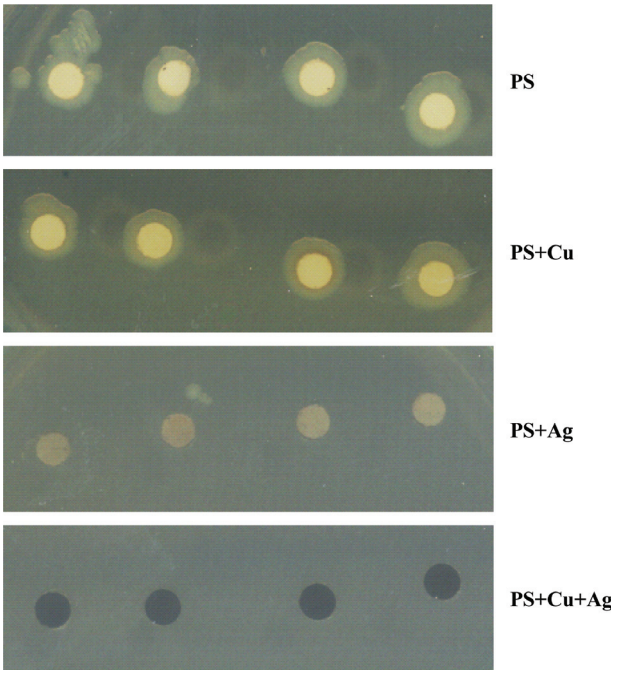

Fig. 15. Biofouling resistant property of membrane surfaces. Author Queries.

that the impregnation of silver on to the polysulfone host matrix make the membrane surface less prone to biofouling, and hence an anti-biofouling membrane was developed. Similar results are obtained with silver embedded polysulfone membrane by the researchers [30].

4. Conclusion

Nanoparticles provide immense opportunities in water treatment applications. We conclude that the disinfectant property of silver nanoparticles can be exploited towards development a biofouling resistant membrane. The way to go about developing an integrated scaled up system using nanoparticles has been illustrated here. It was observed that nanoparticles of copper are leaching out from the host polymeric matrix into gelling medium while they are alone or associated with silver. Hence the possibility of examining and confirming the change in antibiofouling property of silver in presence of copper could not be ascertained. Therefore, presently the research group is engaged in trying out the possibilities of different polymeric matrixes where impregnation of silver–copper mixture can be successful without leaching, and then antibiofouling property of silver alone could be compared with that of silver–copper mixture. The effect of different polymers and size of nanoparticles on the biofouling resistance property of membrane is also under evaluation. Also the behavior and response of membrane surface towards different types of microorganism need to be examined in detail.

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