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# Improvement of membrane system for water treatment by synthesized gold nanoparticles

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**Abstract**

Clean water is an essential requirement for all life and therefore, the societal benefit from effective water treatment methods are significant. There are many different methods to treat contaminated water; one being microfiltration. The surface modification of membranes with nanoparticles one way to address these challenges and hence, improve membrane performance. Recently, successful attempts have been made to deposit the nanoparticles onto the membrane. Gold nanoparticles (AuNps) can be coated on common microfiltration membrane by overnight exposure of the membrane to nanoparticles solution. Membrane's surface can be modified by synthesized AuNps solution, which has an outstanding filtration performance as compared to conventional membranes. In the present study, AuNps supported poly ether sulfone (PES) membrane was characterized by SEM with EDAX analysis. The coated membrane performance was investigated through microfiltration experiment, and the activities were compared with conventional PES membranes. This coating procedure led to increase in the performance of membrane for the application of water treatment.

**Key words**

Gold nanoparticles, Microfiltration, PES membranes, Water treatment

## Introduction

According to the World Health Organization (2009), water scarcity is a growing issue that affects one in three people on every continent. Population growth, urbanization, increased standards of living, and the expansion of industrial activities are exacerbating this issue (Choi *et al*., 2002). Various types of treatment methodologies are available, among these root zone treatment has also been suggested for treating waste water (Deeptha *et al*., 2014). Modification of membrane surface has been suggested recently as a method of enhancing desirable membrane properties or providing new, unique functionalities. To enhance the membrane properties, deposition of membranes by metal nanoparticles has been found. The use of metal nanoparticles for water disinfection is relatively new (Stoimenov *et al.,* 2002). Because of their high reactivity due to the large surface to volume ratio (Barraque, 2003), nanoparticles are expected to play a crucial role in water purification When water becomes an important commodity (Zuhuang, 2003). The immobilization of pectinase enzymes onto the magnetic nanoparticles support is an important tool as it provides distinct advantages including enhanced stability, easy separation, improved catalytic properties and arrest of microbial growth (Ramankannan *et al.,* 2013). Metal nanoparticles such as gold, silver and iron have attracted increasing attention as catalysts and reagents for water treatment because of their unique reactivity with pathogens, pesticides and mercury (Xie *et al*., 2011).Research in nanotechnology promises breakthroughs in areas such as medicine (Datta *et al*., 2006 ; Singh *et al*., 2008) data storage (Menon *et al*., 1999), food industry (Sastry *et al*., 2011), molecular biotechnology (Koehlera *et al*., 2001), computing (Liu *et al*., 2010), defence (Altmann *et al*., 2004) , robotics

(Santoli *et al*., 1997), textiles (Wong *et al*., 2006 ; Qian *et al*., 2004) environment and sanitation (Nowack *et al*., 2008 ; Zhuang *et al*., 2011). Another exciting and promising application of nanotechnology is water purification (Diallo *et al*., 2005).Nanoparticles of gold coated with palladium are effective catalysts for removing tri-chloroethane from groundwater, 2,200 times better than palladium alone. (Dhermendra *et al*., 2008). In the present study, an inventive contribution for surface modification of PES membrane by AuNps has been studied. These modified membranes were capable of removing pollutants and germs efficiently.

## Materials and Methods

**AuNps synthesis : S**ynthesis of AuNps was carried out following the procedure of Zabetakis *et al*. (2012). The pellets were finally re-dispersed in distilled water and air dried to obtain the powdered form of GNPs. The GNPs solution was analysed by Shimadzu double beam spectrophotometer for its maximum Surface Plasmon Resonance. A 0.3 ml of the solution was taken and it was diluted to 3 ml with distilled water and the reading was taken in a double beam spectrophotometer between at 400 to 700 nm (Naheed Ahmad *et al*., 2012). The maximum absorbance peak obtained confirmed the presence of AuNPs in the solution.

**Characterization of gold nanoparticles**

**UV-Vis spectroscopy :** After incubation, the gold nanoparticle solution, which was synthesized by by biological method was analysed by Shimadzu double beam spectrophotometer for its maximum surface Plasmon resonance (SPR). A 0.3 ml of solution was taken and it was diluted to 3 ml with distilled water and absorbance was read at 400 to 800 nm. The maximum absorbance peak obtained confirmed the presence of gold nanoparticles in the solution.

**SEM analysis :** Scanning electron microscope (SEM) technique was employed to visualize the size and shape of Au nanoparticles. A Philips XL30 SEM was used. The SEM samples of aqueous suspension of AuNps were fabricated by dropping the suspension onto clean electric plate and allowing the water to completely evaporate. The dried suspension of gold nanoparticles synthesized by reduction between gold ions and trisodium citrate was analysed under Philips XL30 Scanning Electron Microscope.

**EDAX analysis:** The Energy Dispersive X-ray analysis spectroscopy was used to determine the presence of elemental gold in the synthesized solution. The samples obtained from synthesis process were dried at room temperature and analysed for the composition of samples in the synthesized nanoparticles.

**FTIR analysis :** AuNps synthesized were centrifuged at 10000 rpm and the supernatant were discarded. The pellet was washed with deionised water, and the process was repeated thrice to wash out free proteins and enzymes that did not participate in the capping of AuNps. These pellets were analysed by FTIR. The pellets were scanned on Perkin-Elmer FTIR spectrum in transmittance mode at a resolution of 2 per centimeter.

**Fabrication of AuNps coated membrane :** The physical properties of PES membrane is given in Table 1. The procedure for coating was done following the method of Xie *et al*. (2011). The AuNps used in the membrane modification experiments were established from the amount of reagents used and was in the order of $10^{10}$ particles $ml^{-1}$**.** The PES membranes (size) were soaked in AuNps solution overnight. The membrane attracted the AuNps as apparent by reduced optical properties of the nanoparticles solution remaining, after incubation. In case of overnight immersion the remaining solution became almost transparent. This suggested a strong electrostatic attraction between the AuNps and PES membrane. After incubation, a white membrane acquired a black colour, whose intensity increased after incubation. The PES membranes were washed repeatedly with water to remove any adsorbed ions and were air-dried. The coated PES membranes were characterized by SEM with EDAX analysis.

**Microfiltration experiment :** The coated and uncoated membrane performance were checked by microfiltration process. For microfiltration analysis, laboratory scale microfiltration unit was used. Sampling for physico-chemical analysis, the water samples were collected from local area. All the containers were rinsed with ethanol followed by tap water and distilled water before sample collection. The physical and chemical (Table 2) parameters were analysed according to the standard methods (APHA, 2012). Fig 1 shows the schematic diagram of microfiltration lab scale unit used for the treatment of raw water drawn from the Madhuranthagam Lake, Tamilnadu, India. Peristaltic pump was used for feed. The flow of various streams was measured by rota meters or disc meters, bourdon gauges were used to measure the pressure at the entrance and exit to the membrane set up. The samples were stored in refrigerator without any pre-treatment before being used in the microfiltration system. The maximum storage time was less than 2 weeks. The quality of raw water is presented in Table 3. The membrane filtration was carried out in a lab scale microfiltration apparatus using PES membrane. Two types of filtration study was carried out. One using uncoated PES membrane, other AuNps coated PES membrane. Experiments were conducted with a feed volume of 1 litre for both filtration studies. Permeate variation were studied for

**Table 1 :** Properties of PES Membrane

| Membrane attribute | PES nominal or average values |
|---|---|
| Pore size | 0.2 µm |
| Porosity | 70-75% |
| Thickness | 129.5-162.6 µm |
| Solvent compatibility | Broadly compatible with wide rangeof aqueous and organic solvents. |
| Mechanism of binding | Hydrophobic |
| Water Flow | 19.3-34.6 ml $min^{-1}$ $cm^{-2}$@ 0.7 bar, 10 psi |

**Table 2 :** Standard values for physical and chemical properties of water

| Parameters | Particulars | Permissible limits Indian standards (IS) 10500,2012 |
|---|---|---|
| Physical | Colour (Hazen Units) | 15 |
| | Odour | Agreeable |
| | Turbidity (NTU) | 5 |
| | Electrical Conductivity @ 25$^{R°}$C (Micromhos/cm) | - |
| | pH value at 25$^{R°}$C | 6.5-8.5 |
| Chemical (mg $l^{-1}$) | Total Hardness as $CaCo_3$ | 600 |
| | Calcium Hardness as $CaCo_3$ | - |
| | Magnesium Hardness as $CaCo_3$ | - |
| | Magnesium as Mg | 100 |
| | Calcium as Ca | 200 |
| | Alkalinity as $CaCo_3$ Phenolpthalin total | 600 |
| | Chlorides as $Cl^-$ | 1000 |
| | Sulphates as $SO_4^{2-}$ | 400 |
| | Total iron as Fe | 0.3 |
| | Silica as $Sio_2$ | - |

mg $l^{-1}$: milligrams per litre; NTU: number of transfer units

both filtration process. The physical and chemical parameters were analysed for treated water using AuNps coated membrane through microfiltration experiment and those limits were compared with permissible limit as per IS 10500, 2012,second revision.

## Results and Discussion

### Characterization of AuNps

**Visual observations :** After addition of trisodium citrate to gold solution, the colour changed from colourless to deep wine red colour indicating formation of AuNps. This was due to fabrication of AuNps with the molecular assistance of reducing agents present as trisodium citrate (Zabetakis *et al.*, 2012).

**Table 3 :** Characteristics of raw water

| Parameter | Range |
|---|---|
| Turbidity (NTU) | 5.0 |
| pH | 7.9 |
| TDS (mg $l^{-1}$) | 2250 |
| colour (Hazen units) | Slightly brackish |

**UV analysis :** Equivalent amount of suspension was diluted in a constant volume of de ionized water and subsequently analysed at room temperature. The progress of reduction reaction of metal ions was monitored with different reaction times (Fig. 2). The absorption spectrum of AuNps ranging from 400 nm to 694 nm with reaction time of 30, 60 and 90 min, and the peak was found between at ~ 540 nm to ~ 550 nm. Similar peak value was obtained by Naheed ahmad *et al*. (2012) for AuNps.

**SEM analysis :** Fig. 3 shows typical SEM micrographs of synthesized AuNps. These images suggest that the particles were polydisperse and were mostly spherical in shape. An agglomerated nanoparticles were observed in the SEM graph, variation in particle sizes and average size was estimated was 19-30 nm. These results are in accordance with Tamizhamudu *et al*. (2011). Where, the sizes were 500,200,100 and 50 nm are obtained using *Memecylon edule* leaf extract.

**EDAX analysis :** The EDAX result demonstrated strong peaks of Au at 2.0keV and also confirmed the existence of C

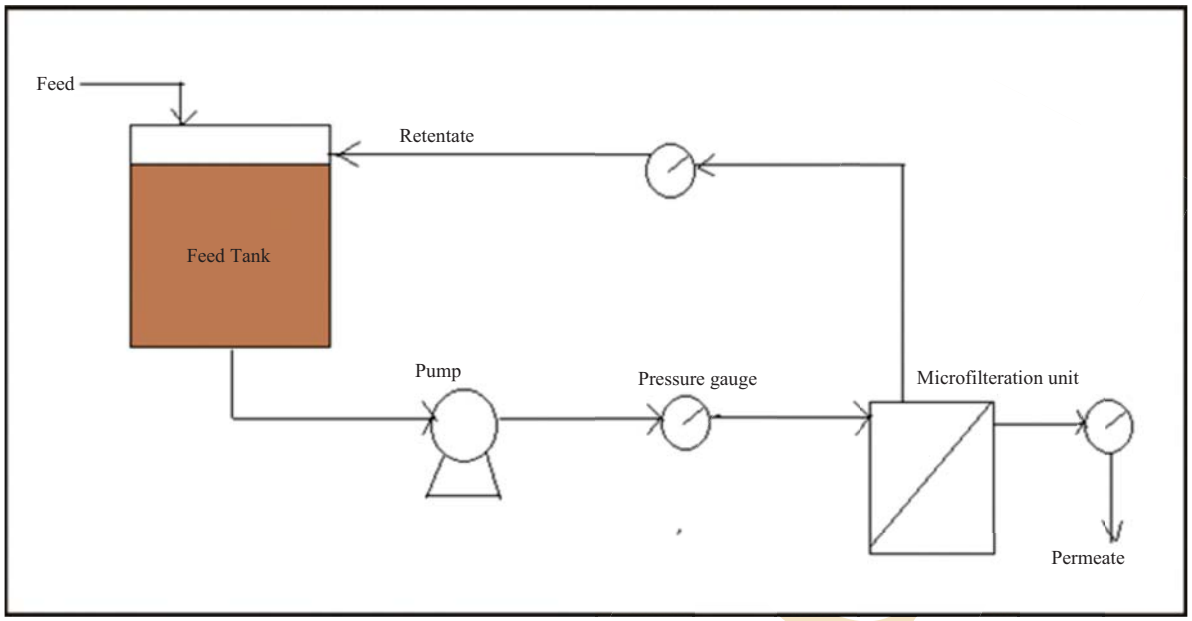



**Fig. 1 :** Microfiltration set up

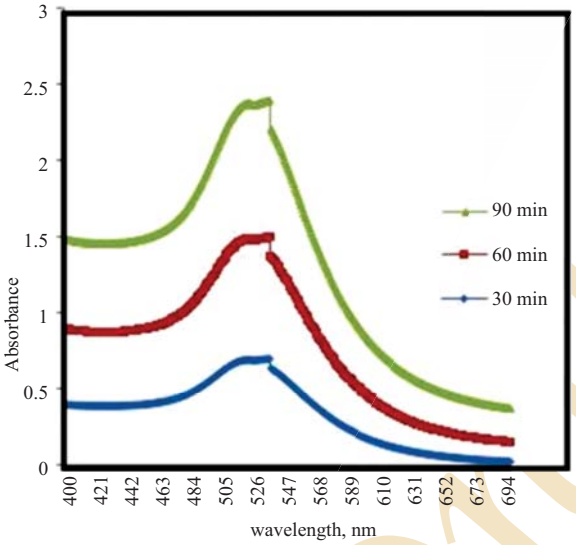



**Fig. 2 :** UV –Vis Spectrum of synthesized AuNps

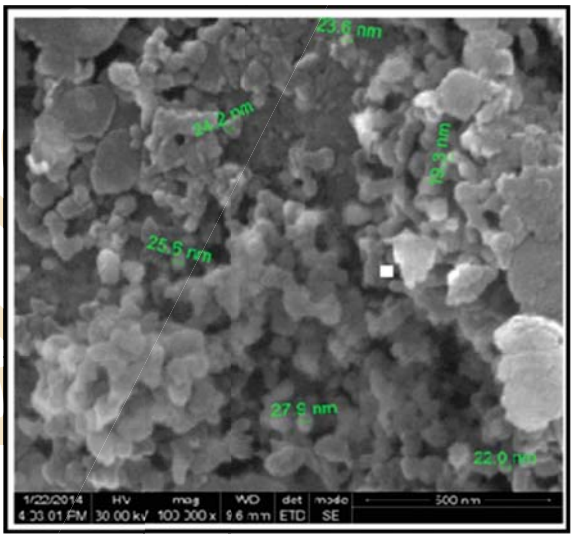
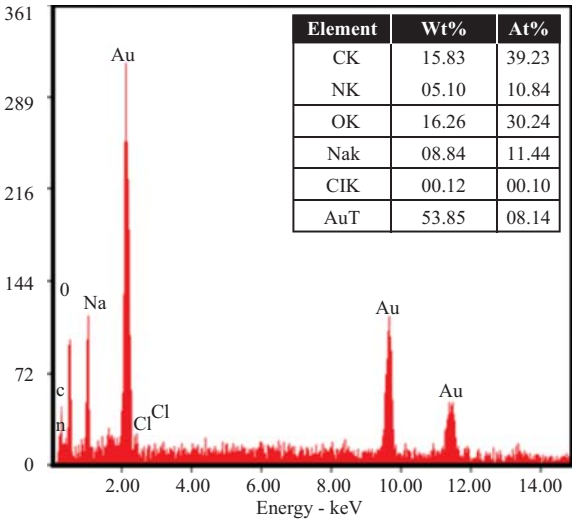



**Fig. 3 :** SEM micrograph of synthesizedAuNps

and O indicating the adsorption of citrate on the surface of the gold nanoparticles. The Cu signals were due to the use of a copper grid, and the appearance of Cl was due to the existence of $AuCl_4^-$ ions. The inset picture shows 53.85 % AuNps present in the synthesized sample (Fig. 4). Zhao *et al*. (2014) investigated the glucomannan –mediated facile synthesis of AuNps to increase the stability of AuNps. Their study revealed the strong peaks of Au at 2.195 Kev and also confirmed the presence of C and O.

**FTIR analysis :** FTIR absorption spectra can provide information about the chemical change of functional groups involved in the reduction process. Fig. 5 shows FTIR spectra of synthesized AuNps .Addition of gold solution to sodium citrate revealed strong bands at 3411,2151,1652 and 782 $cm^{-1}$.The bands corresponded to N-H (amines), -C=C- (alkynes), -C=C- (alkenes ) and C-H (alkenes). Padma *et al.* (2010) reported that FTIR spectrum of AuNps prepared from the aqueous extract of *Mirabilis jalapa* flowers, suggested that




| Element | Wt% | At% |
|---|---|---|
| CK | 15.83 | 39.23 |
| NK | 05.10 | 10.84 |
| OK | 16.26 | 30.24 |
| Nak | 08.84 | 11.44 |
| CIK | 00.12 | 00.10 |
| AuT | 53.85 | 08.14 |

**Fig. 4 :** EDAX spectrum of synthesized AuNps

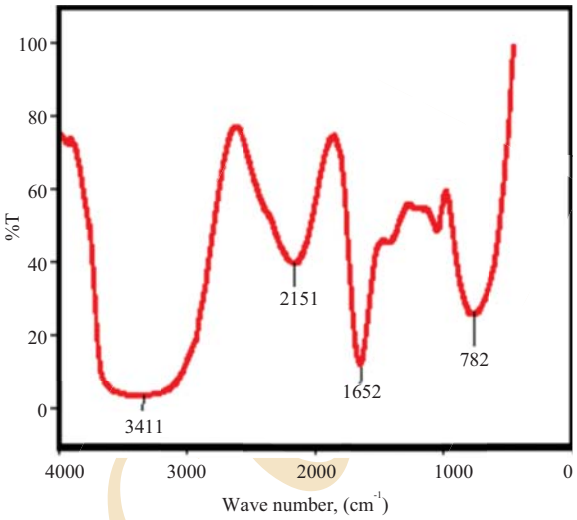



**Fig. 5 :** FTIR spectrum of synthesizedAuNps

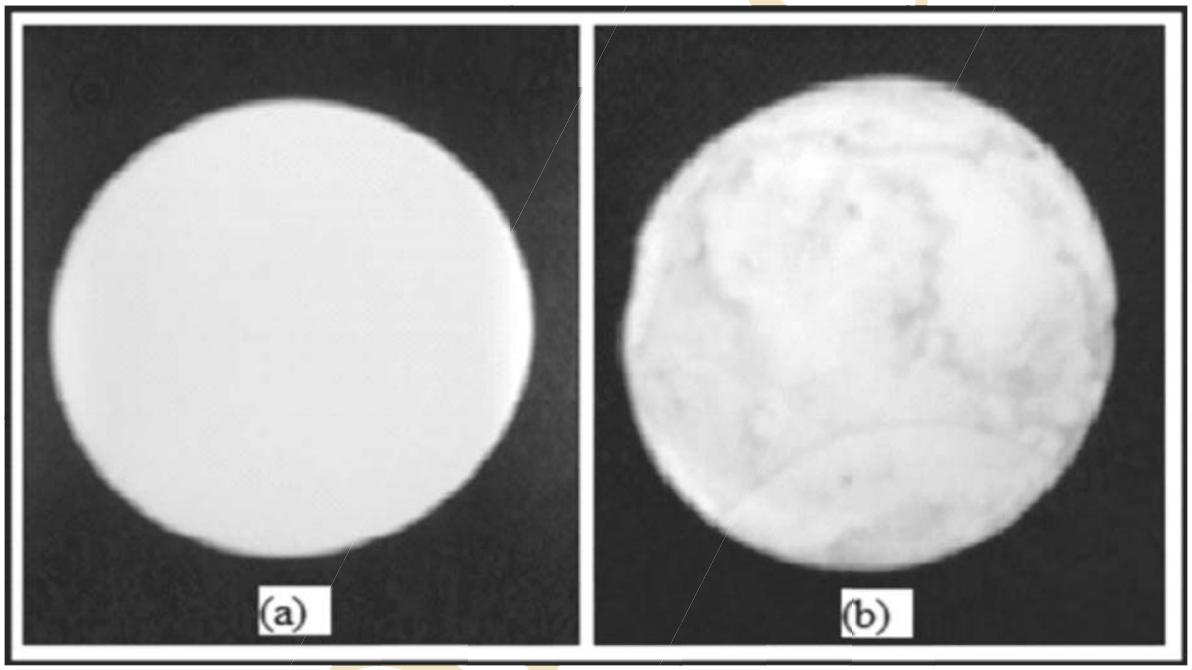


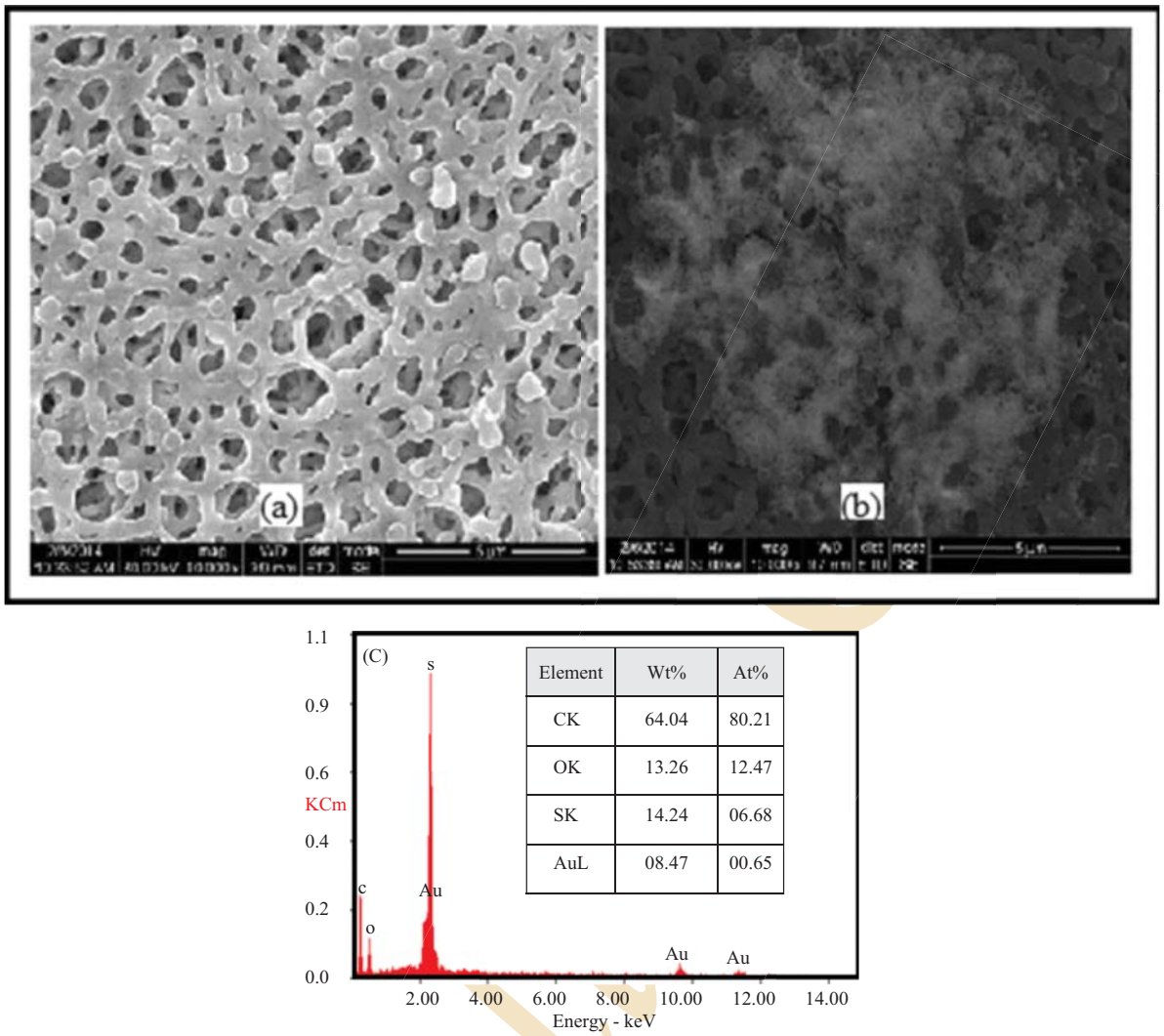

**Fig. 6 :** Visual observation of (a) uncoated membrane (b) AuNps coated membrane

the flower extract acted as a reducing agent and encapsulating cage of the AuNps.

**Membrane characterization**

**Visual observations :** As a result of visual observation, a white membrane (Fig. 6a) acquired black colour (Fig.6b), whose intensity increased with incubation. This suggested that the membrane attracted AuNps and thereby, reduced the optical properties of the remaining solution (Xie *et al*., 2011).

**SEM with EDAX analysis:** To confirm the presence of AuNps in the membranes, SEM imaging was carried out. Fig. 7b shows a highly non - uniform distribution of nanoparticles within the membranes, despite a relatively uniform black colour was observed by visual inspection. A simple calculation, using the total membrane area and density of particles made it possible to estimate the number of particles,




| Element | Wt% | At% |
|---|---|---|
| CK | 64.04 | 80.21 |
| OK | 13.26 | 12.47 |
| SK | 14.24 | 06.68 |
| AuL | 08.47 | 00.65 |

**Fig. 7 :** SEM image of (a) uncoated membrane (b) AuNps coted membrane (c) EDAX of AuNps

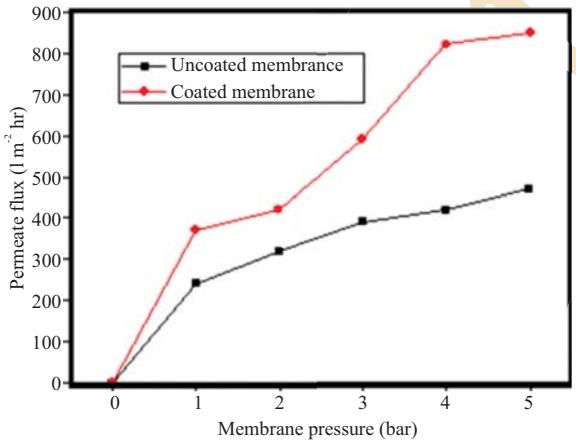



**Fig. 8 :** Variation in permeate flux with membrane pressure

deposited in the membrane (Xie *et al.,* 2011). The EDAX analysis (Fig. 7c) of the membrane further confirmed the presence of AuNps in the membrane.

**Microfiltration test**:

**Permeate quality**: In order to investigate the ability of the membrane to remove particles, microorganisms of retentate and permeate were collected during various runs. The results of physical, chemical and microbiological analyses are listed in Tables 3 to 6. These results were compared with the permissible limits of IS 10500 (2012). The results seemed to be highly satisfactory, as physical, chemical parameters were completely reduced as compared to uncoated membrane. Table 6 shows that the microorganisms were completely was removed and this removal only depended on AuNps coated

**Table 4 :** Physical characteristics of water before and after coating

| Parameters | Uncoated membrane | Permissible limits (IS 10500, 2012) | Coated membrane |
|---|---|---|---|
| | | **Physical quality** | |
| Colour (Hazen Units) | <10.0 | 15 | <10.0 |
| Odour | Agreeable | Agreeable | Agreeable |
| Turbidity(NTU) | 2.1 | 5 | 1.3 |
| Electrical Conductivity@25°C ( Micromhos/cm) | 1941 | - | 1895 |
| pH Value at 25° C | 7.72 | 6.5-8.5 | 7.86 |

**Table 5 :** Chemical characteristics of water before and after coating

| Parameters | Uncoated membrane | Permissible limits (IS 10500, 2012) | Coated membrane |
|---|---|---|---|
| | | **Chemical quality** | |
| Total Dissolved Solids | 1941 | 2000 | 1137 |
| Total hardness as $CaCO_3$ | 500 | 600 | 450 |
| Calcium hardness as $CaCO_3$ | 210 | - | 200 |
| Magnesium hardness as$CaCO_3$ | 290 | - | 250 |
| Magnesium as Mg | 70 | 100 | 60 |
| Calcium as Ca | 84 | 200 | 80 |
| Alkalinity as $CaCO_3$ | 90 | 600 | 32 |
| Chlorides as $Cl^-$ | 223 | 1000 | 223 |
| Sulphates as $SO_4^{2-}$ | 76 | 400 | 73 |
| Total iron as Fe | 0.17 | 0.3 | 0.11 |
| Silica as $Sio_2$ | 44 | - | 18 |
| Aurum as Au | - | - | BDL(D.L:10ppb) |

**Table 6 :** Microorganism retention

| Microorganism in 100 ml | Retentate(100 ml) | Permeate(100 ml) | Retention (%) |
|---|---|---|---|
| E.coli | $4 \times 10^6$ | Nil | 100 |
| Fecal coliforms | 20 | Nil | 100 |
| Total coliforms | 25 | Nil | 100 |

PES membrane. Fig. 8 reveals that the permeate flux appeared increase with the membrane pressure. But it gave a high flux rate for coated membrane. While the membrane pressure increased from 0 to 5, the normal membrane gave maximum flux rate of 470 $Lm^{-2}$ $h^{-1}$, whereas, the AuNps coated membrane gave the maximum rate of 850 $Lm^{-2}h^{-1}$. It indicated that the 56% of flux increased in AuNps coated membrane (Bernd, 2010).

It is clear that AuNPs coated membrane provided double the amount of increasing flux efficiency. Compare to improved flux efficiency, there was no point of cost for membrane modification. However, a trace amount of nanoparticles was only required for one membrane for coating process. Therefore, not much cost was required for membrane modification using AuNPs. Bottino *et al.* (2001) examined water treatment using ceramic microfiltration. They suggested that the long term performance and more productive was necessary for polymeric membranes.

Studies are to be continued in future to obtain various concentrations of coating of AuNps onto PES membrane for long term performance and operating at the highest level of foulants. Membrane filtration of lake water through PES membrane has proved to be useful for drinking water production. Suspended solids were completely removed along with the microorganisms and algae. The results proved that the coating membrane provided greater efficiency as compared to uncoated membrane in all the aspects of characteristic of drinking water. The permeate flux also increased double for coated membrane. Therefore, a good improvement in membrane process was achieved due to

AuNPs coating for water treatment. Further, studies are in progress to obtain treatment cost at more competitive levels. For this aim, long term performance of less expensive and more productive PES membrane will be investigated in order to obtain enough information for designing continuous AuNPs coated membrane reactors. It is suggested that the AuNps supported PES membrane might be used in future at large scale water purification in microfiltration system.

## References


Barraque, B.: Past and future sustainability of water policies in Europe. *Nat Res. Forum,* **27**,200–211 (2003).

Bernd, N.: Pollution prevention and treatment using nanotechnology. *Nanotechnology,* **2**, 1-15 (2010).

Bottino, A., C. Capannell, A. DelBorgh, M. Colombinob and O. Coniob: Water treatment for drinking purpose: Ceramic microfiltration application. *Desalination,* **141**, 75-79 (2001).

Choi, J.G., T.H. Bae, J.H. Kim, T.M. Tak and A. Randall: The behavior of membrane fouling initiation on the cross flow membrane bioreactor system. *J. Membr. Sci.*, **203**,103-113 (2002).

Datta, R. and S.S. Jaitawat: Nanotechnology- the new frontier of medicine. *Med. J. Arm. For. Ind.*, **62**, 263- 268 (2006).

Deeptha, V.T., J.S. Sudarsan and G. Baskar: Performance and cost evaluation of constructed wetland for domestic waste water treatment. *J. Environ. Biol.*, **36**,1071-1074 (2015).

Dhermendra, K., J. Tiwari, Behari and Prasenjit Sen: Application of nanoparticles in waste water treatment. *World App. Sci. J.*, **3,** 417-433 (2008).

Diallo, M.S., S. Christie, P. Swaminathan, J.H. Johnson and W.A. Goddard: Dendrimer enhanced ultra-filtration recovery of Cu (II) from aqueous solutions using Gx-NH2-PAMAM dendrimers with ethylene diamine core. *Environ. Sci. Technol.,* **39**, 1366-1377 (2005).

Jurgen, A and M.A. Gubrud: Discovering the nanoscale. 1st Edn. IOS press, Amsterdam (2004).

Koehlera, M. and S. Diekmann: Biomolecular nanotechnology. *Mole. Biotechnol.*, **82**, 1-2 (2001).

Liu, B.: Architecture exploration of crossbar based nanoscale reconfigurable computing platforms. *Nano Communi. Networks*, **3**, 232-241 (2010).

Menon, A.K. and B.K. Gupta: Nanotechnology: A data storage Perspective. *Nanostruct. Mat.*, **12**, 1117-1125 (1999).

Naheed, A., S. Seema and R. Radheshyam: Rapid green synthesis of silver and gold nanoparticles using peels of *Punica granatum. Adv. Mat. Lett*., **3** ,376-380 (2012).

Padma, S.V. and D. Bajpai: Preparation of gold nanoparticles from *Mirabilis jalapaflowers*. *Ind. J. Biochem. Biophy.,* **47**, 157-160 (2010).

Qian, L. and J.P. Hinestroza: Application of Nanotechnology for high performance textiles. *J. Text. App. Technol. Manag.*, **4**, 1-7 (2004).

Santoli, S.: Nano-to-micro integrated single-electron biomacromolecular electronics for miniaturizedrobotic untethered flying observers *Acta Astronautica*., **41**, 4-10, 279- 287 (1997).

Sastry, R.K., H.B. Rashmi and N.H. Rao: Nanotechnology for enhancing food security in India. *Food Policy,* **36**, 391-400 (2011).

Singh, C., K.B. Ritesh, P.K. Naik and H. Singh: Biocompatible synthesis of silver and gold nanoparticles using leaf extract of *Dalbergia sissoo*. *Advan. Mater. Lett.*, **3**, 279-285 (2012).

Stoimenov, P.K, R.L. Klinger, G.L. Marchin and K.J. Klabunde: Metal oxide nano particles as bactericidal agent. *Sup. Part. Technol.,* **18**, 6679-6686 (2002).

Tamizhamudu, E., D. Kantha Arunachalam: *Memecylon edule* leaf extract mediated green synthesis of silver and gold nanoparticles. *Inter. J. Nanomed.,* **6**, 1265-1278 (2011).

Wong, Y.W.H., C.W.M. Yuen, M.Y.S. Leung, S.K.A. Ku and H.L.I. Lam: Selected applications of Nanotechnology in Textiles. *AUTEX Rese. J.*, **6**, 34-40 (2006).

World health organization Water Quality: Guidelines, Standards and Health: Assessment of Risk and Risk Management for Water-related Infectious Disease http://www.who.int/water_sanitation_health/dwq/w(2009).

Xie, F., T. Drozdowicz-Tomsia, T. Shtoyko and E.M. Goldys: Silver and gold nanoparticle coated membranes applied to protein dot blots. *J Nanopart.,* **13**, 613–624 (2011).

Zabetakis, K., W.E. Ghann, S. Kumar and M. Daniel: Effect of high gold salt concentrations on the size and polydispersity of gold nanoparticles prepared by an extended Turkevich–Frens method. *Gold Bull.,* **45**, 203–211(2012).

Zhao, G., S. Rongxin, H. Renliang, W. Qi1 and H. Zhimin: Glucomannan-mediated facile synthesis of gold nanoparticles for catalytic reduction of 4-nitrophenol. *Nano Scale Res. Lett.,* **9**, 404 (2014).

Zhuang, J. and R.W. Gentry: Environmental application and risks of nanotechnology: A balanced view biotechnology and nanotechnology: minding and managing the potential threats around us. *ACS Symposium Series*, **3**, 41–67 ( 2011).

Zuhuang, J.: Bactericidal nano-silver cloth and its making process and use. Patent number CN 1387700 (2003).