



Multifunctional Nanocomposite Membranes for Treatment of Chromium from Wastewater

Final Report 2019



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EXECUTIVE SUMMARY

The scarcity of clean water is a global issue that poses serious challenges to the survival of all living species. The membrane technology has gained considerable attention to address this issue. The polymer nanocomposite membranes (PNCMs) are the most favorable choice in membrane technology. These are low cost, eco-friendly, and energy-efficient membrane materials with operational flexibility and feasibility. In this study, copper and silver nanoparticles were separately immobilized on the pristine sepiolite by the green chemical reduction method. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), wide-angle x-ray diffraction (WAXD) and energy-dispersive X-ray spectrometry (EDS) analysis were used for characterization of copper-containing sepiolite (Cu/SP) and silver-containing sepiolite (Ag/SP). Transmission electron and scanning electron micrographs demonstrated that the fiber morphology of pristine sepiolite remained intact after the incorporation of Cu and Ag nanoparticles. FTIR, WAXD, and EDS analysis confirmed the successful grafting of copper, copper oxide, and silver and silver oxide nanoparticles on the sepiolite fibers. Both Cu/SP and Ag/SP demonstrated significant antimicrobial potential against E. coli and P. aeruginosa. Three sets of polymer nanocomposite membranes, i.e., polyvinyl alcohol/pristine sepiolite (PVA/ SP), copper-containing sepiolite/polyvinyl alcohol (Cu/SP@PVA) and silver-containing sepiolite/polyvinyl alcohol (Ag/SP@PVA) were prepared by a simple, cost-efficient, and eco-friendly phase inversion method. Tetraethyl orthosilicate (TEOS) was used as a crosslinker. During the preparation of polymer nanocomposite membranes, the optimization of different parameters, including the concentration of crosslinker, polymer, and sepiolite, was carried out. The polymer nanocomposite membranes were characterized by SEM, FTIR, WAXD, and EDS analysis. Well dispersed pristine sepiolite fibers and metal nanoparticles loaded sepiolite fibers were evident in the scanning electron micrographs of PVA/SP, Cu/SP@PVA, and Ag/SP@PVA nanocomposite membranes. FTIR analysis of Cu/SP@PVA and Ag/SP@PVA nanocomposite membranes demonstrated the formation of siloxane and coordinated bonds between polymeric matrix and metal nanoparticle containing sepiolite. WAXD diffractograms of PVA/SP, Cu/SP@PVA-3, and Ag/SP@PVA-3 nanocomposite membranes showed the retention of a characteristic diffraction peak at $2\theta=7.30^{\circ}$ (110) lattice plane, as a result of complete exfoliation of sepiolite bundles into sepiolite fibers within the polymer matrix. Mechanical properties of nanocomposites were significantly increased due to the incorporation of pristine sepiolite as well as metal nanoparticle containing sepiolite fibers in comparison to pure PVA alone. A higher degree of crosslinking led to brittleness and a decline in mechanical properties of polymer nanocomposite membranes. A significant Cu nanoparticle leaching was detected from nanocomposite

membranes using deionized water in comparison to Ag nanoparticles. Batch adsorption studies were carried out for hexavalent chromium Cr (VI) uptake onto nanocomposite membranes to envisage the effects of initial pH, adsorbent dose, contact time, and initial chromium ion concentration. The adsorption capacity (mg/g) and Cr removal (%) of PVA/SP-3, Cu/SP@PVA-3, and Ag/SP@PVA-3 nanocomposite was monitored. Among all, PVA/SP-3 nanocomposite membranes are the most suitable choice with 99% ability to remove Cr (VI) ions under optimized conditions (pH = 3, adsorbent dose = 0.01 g, contact time = 10 minutes; initial chromium ion concentration = 60 ppm). The reusability of the PVA/SP-3 membrane was assessed for five adsorption and desorption cycles. The Cu/SP@PVA and Ag/SP@PVA nanocomposite membranes demonstrated excellent antibacterial activity against S. aureus, B. cereus, E. coli, and P. aeruginosa present in simulated contaminated wastewater samples. The Cu/SP@ PVA and Ag/SP@PVA nanocomposite membranes could be successfully reused after daily inoculations and subsequent washing, allowing up to 5 cycles with <99.999% CFU removal. Thus, the developed nanocomposite membranes are a useful choice for the removal of heavy metals and biofouling.

1. INTRODUCTION

Chromium (Cr) is a vital constituent of our environment. It holds the sixth position in the earth's crust due to its abundance. However, Cr is one of the most notorious heavy metals due to its persistence and non-degradability in the environment. It frequently comes into water and soil from the industrial effluents of leather tanning, automobile refinishing, electroplating, metal processing, film processing, steel, and alloys manufacturing industries, as well as from mining of chromium ores (Kotaś and Stasicka, 2000; Igbal and Edyvean, 2004; World Health Organization, 2011; Moraetis et al., 2012). There are different oxidation states of Cr, such as Cr (II), Cr (III), Cr (V), and Cr (VI), while the most stable states of Cr ion are Cr (III) and Cr (VI) (Hamilton et al., 2018). The hexavalent chromium, Cr (VI) is considered as the most toxic form of chromium salts due to its solubility and mobility in the environment. The World Health Organization (WHO) stated that the maximum allowable concentration of Cr (VI) in drinking water is 0.05 mg/L (World Health Organization, 2003). The Cr (VI) is a potent mutagen and carcinogen (Ackerley et al., 2006; Rajput et al., 2016). Other adverse effects of Cr (VI) on human health include ulcerations, diarrhea, dermatitis, and allergic skin reactions (Basketter et al., 2001). Currently, natural zeolites (Yao et al., 2019), precipitation (Harper and Kingham, 1992), ultrafiltration (Muthumareeswaran et al., 2017), coagulation (Balasubramanian and Madhavan, 2001), ion exchange and adsorption (Chutia et al., 2009; Mandal et al., 2011), and biosorbent (Netzahuatl-Muñoz et al., 2015) are used for the removal of heavy metals from wastewater. Nevertheless, all these methods have drawbacks, especially regarding efficiencies and costs.

The polymeric nanocomposite membrane (PNCM) technology is considered as a powerful emerging tool for the removal of heavy metals and other pollutants from wastewater due to its efficacy, low-cost and ease of scale-up (Yin and Deng, 2015) (Nasir et al., 2019). PNCMs are developed by the addition of nanofiber/nanoparticle onto the various supporting polymeric matrix. The PNCM demonstrated a significant enhancement in mechanical and antibacterial properties as compared to the polymer alone. Polyvinyl alcohol (PVA) is a low-cost polymer. The PVA is widely used for the preparation of PNCM due to its chemical stability, cost-effectiveness, film-forming capability, outstanding mechanical and chemical features (Peng et al., 2010; Peng et al., 2011). However, the semi-crystallinity and hydrophilicity of PVA are the major obstacles in its commercialization for wastewater treatment. Therefore, the stability of PVA membranes was enhanced with the use of crosslinking agents for commercial wastewater treatment plants in the past (Peng et al., 2011; Ahmad et al., 2012). There are several reports on the preparation of PVA composites/nanocomposites membranes using montmorillonite (Raheel et al., 2015; Karimi and Wan Daud, 2017), sepiolite (Alkan and Benlikaya, 2009), silica (Wang et al., 2008), TiO2 (Liu et al., 2019), and magnetic nanoparticles.

Fouling is a key issue in membrane technology (Le-Clech et al., 2006; Ke et al., 2013). The foulants are either directly adsorbed on the membrane surface or trapped into the pores/matrix of the membrane. Moreover, biofouling is caused by irreversible binding and reproduction of bacterial cells followed by biofilm formation, and ultimately, the biofilm covers the entire surface of the membrane, a powerful approach for hindering biofouling is thus to confer the membrane surface with antibacterial features (Yeon et al., 2009; Chen et al., 2012). Additionally, the high cost associated with material replacement due to fouling hindered the widespread application of membrane technology for wastewater treatment (Meng et al., 2009). Hence, the nanocomposite membrane with outstanding mechanical features and excellent antibacterial properties is mandatory for the commercialization of membrane technology.

Sepiolite is a member of the 2:1 phyllosilicate family. The sepiolite is a natural hydrated fibrous magnesium silicate. The structural formula of sepiolite is Si12Mg8O30(OH)4(OH2)4.8H2O. The sepiolite demonstrated needle morphology with an alternation of tunnels and blocks. These blocks are in the ribbon form that is held together to form the open channels (tunnels), which are filled with the zeolitic water molecules and exchangeable ions (Konta, 1993). There is a central octahedral magnesium/magnesium hydroxide layer, which is sandwiched between two layers of tetrahedral silica sheets. Each of the Mg2+ cations found at the corner of the octahedral sheet is bonded to the two molecules of coordinated water molecules. There is no continuous octahedral sheet in sepiolite (Aşkın and Yažici, 2005), while there are several Si-OH groups (2 Si-OH groups/nm2) available on the external surface of sepiolite (Rebitski et al., 2018). The sepiolite has good sorption capacity due to high surface area (320 m2/g) and good porosity that makes it a suitable candidate for wastewater treatment (Ruiz-Hitzky, 2001; Al-Ani et al., 2018). Recently, these silanol groups have been used to immobilize different nanoparticles on the sepiolite surface. Sepiolite has been used as a platform for simultaneous immobilization of ZnO (Hassan et al., 2016), zinc oxide and magnetite (ZnO/Fe3O4) (Akkari et al., 2017), titanium dioxide/zinc oxide (TiO2/ZnO) (Vaizoğullar, 2017), core-shell silver @ platinum (Ag@ Pt) (Ma et al., 2017) and gold (Au) (Pecharromán et al., 2009) nanoparticles for different applications in daily life. Sepiolite has been frequently used as an adsorbent for the removal of different metal ions, i.e., Pb, Zn, Cu, Cr, Mn, and Cd from the wastewater (Kocaoba, 2009).

In the present study, copper and silver nanoparticles containing sepiolite (Cu/SP, Ag/SP) were prepared by a simple chemical reduction method. The PVA/SP/Cu and PVA/SP/Ag nanocomposite membranes were developed by phase inversion technique. Tetraethyl orthosilicate (TEOS) was used as a crosslinker. The structural properties of PVA/SP/Cu and PVA/SP/Ag nanocomposite membranes were evaluated by Fourier

transform infrared spectroscopy, wide-angle x-ray diffraction analysis, scanning electron microscopy, and energy-dispersive X-ray spectrometry. Mechanical properties of PVA/SP/Cu and PVA/SP/Ag nanocomposite membranes were determined. The release studies of metal-based nanoparticle from PVA/SP/Cu and PVA/SP/Ag nanocomposite membranes were carried out by inductively coupled plasma mass spectrometry. The regeneration studies of membranes were also done. Antimicrobial assays of treated wastewater were evaluated by broth dilution assay. Adsorption studies of Cr (VI) by PVA/SP/Cu and PVA/SP/Ag nanocomposite membranes was also carried out under in-vitro conditions

1.1 Objectives of the Project

The goal of the present research project is to develop a multifunctional nanocomposite membrane containing PVA/SP/Ag and PVA/SP/Cu nanoparticles by phase inversion technique.

- i. Preparation and characterization of copper and silver nanoparticles containing sepiolite.
- ii. Optimization of parameters for fabrication of PVA/SP/Cu and PVA/SP/Ag nanocomposite membranes by phase inversion technique.
- iii. Characterization of mechanical and antibacterial properties of PVA/SP/Cu and PVA/SP/Ag nanocomposite membranes.
- iv. Metal-based nanoparticle release studies from PVA/SP/Cu and PVA/SP/Ag nanocomposite membranes.
- v. Antimicrobial bioassays of treated wastewater.
- vi. Adsorption studies of Cr (VI) by PVA/SP/Cu and PVA/SP/Ag nanocomposite membranes under in-vitro conditions.

2. METHODOLOGY

2.1 Materials

Polyvinyl alcohol (PVA) ($M_w = 146,000-186,000$), tetraethyl orthosilicate (TEOS), copper nitrate [Cu(NO₃)₂], silver nitrate (AgNO₃), glucose, sodium hydroxide, potassium dichromate ($K_2Cr_2O_4$), hydrochloric acid and ethanol were obtained from Sigma-Aldrich, Germany. Sepiolite (SP) was purchased from Spain. PVA was used as a polymeric matrix. TEOS was a crosslinking agent. The Cu(NO₃)₂, and AgNO₃ was used as precursor salt for the synthesis of copper and silver nanoparticles. The glucose was used as a reducing agent. Deionized water (stakpure, Germany) was used in all experiments.

2.2 Bacterial Strains

Gram-negative bacterial strains, i.e., *Pseudomonas aeruginosa* ATCC 27853, *Escherichia coli* ATCC11775, and Gram-positive bacterial strains, including *Staphylococcus aureus* ATCC 25923 and *Bacillus cereus* FA11 JN593008, were used in this study. *Bacillus cereus* FA11 JN593008 was isolated from soil (Masood et al., 2012), and the other three bacterial strains were obtained from the American Type Culture Collection. All these strains were preserved at 4°C until use.

2.3 Synthesis of Cu/SP and Ag/SP

The Cu nanoparticles were grown on the sepiolite surface by the chemical reduction method. About 10 g of pristine sepiolite was dispersed in deionized water. Aqueous copper nitrate (1 g) solution was added to the sepiolite suspension under constant stirring. Then, 10 mL of glucose (0.2 M) solution was added into this suspension, and it was stirred at 100 °C for 35 min. The pH of the suspension was raised to 12 using 1 M NaOH. The solution turned brick red due to the formation of Cu/SP. This copper loaded sepiolite was coded as Cu/SP.

The same procedure was used for the preparation of Ag/SP. Briefly, 10 g of pristine SP was dispersed in deionized water. An aqueous solution of $AgNO_3$ (1 g) was added to the SP suspension under constant stirring. Then, 10 mL of glucose (0.2 M) solution was added into this suspension, and the suspension was stirred at 100 °C for 35 min. The pH of the suspension was raised to 11 using 1 M NaOH. The solution turned greenish as a result of the formation of Ag/Sep.

The obtained suspension of Cu/SP and Ag/SP was centrifuged at 10,000 rpm for 3 min and washed with deionized water until neutral pH was obtained. The sample was dried in a vacuum heating oven at 40 °C for three hrs.

2.4 Characterization Studies

The change in color of Cu/SP and Ag/SP was monitored, and their structural characterization of Cu/SP and Ag/SP was done by Fourier transform infrared (FTIR) spectrophotometer (Nicolet 6700, Thermo Electon Crop, Maritta). The FTIR spectrum was recorded using an attenuated total reflectance mode in a range from 4000-400 cm⁻¹ at 100 scans and a resolution of 4 cm⁻¹. The wide-angle x-ray diffractometer (X'Pert Pro PANalytical) was used to evaluate the crystal structure of pristine sepiolite. Cu/SP, and Ag/SP using CuK α radiation by keeping the current, voltage and scanning rate at 36 mA, 36 kV and 0.5 degrees/sec, respectively. The morphologies of Cu/ SP and Ag/SP were determined by scanning electron microscope (VEGA3 TESCAN) and transmission electron microscope (JEOL JEM-1010). The samples were coated with gold (Au) to make them conductive before analysis. The elemental analysis of pristine sepiolite, Cu/SP, and Ag/SP was done by SEM (VEGA3 TESCAN). The particle size, polydispersity index, and zeta potential of pristine sepiolite, Cu/SP, and Ag/SP were also evaluated by using Zeta Sizer: Nano ZS (Malvern Instruments, UK). The antimicrobial activity of Ag/SP and Cu/SP nanoparticles was determined against Pseudomonas aeruginosa ATCC 27853 and Escherichia coli ATCC11775. The number of bacterial cells in sterilized PBS was adjusted to 1.5×10⁸ cells per mL. About 10fold serial dilutions were made in sterilized PBS. Different concentrations (10, 7.5, 5, 4, 3, 2, and 1 mg/mL) of Ag/SP and Cu/SP nanoparticles were added to test tubes containing 18 h old inoculum having 1.5×10⁸ cells per mL. About 2 µL of each dilution was spotted on nutrient agar plates, and colony-forming unit per mL (CFU/ mL) was counted (Thomas et al., 2015).

2.5 Preparation of Nanocomposite Membranes

The PVA/SP nanocomposite membranes were prepared by phase inversion method with some modification (Ahmad et al., 2012). Briefly, PVA was dissolved in distilled water at 100°C for 3 h. An appropriate amount of aqueous dispersion of sepiolite was added into the PVA solution. The mixture was stirred at room temperature until a homogeneous solution was formed. Crosslinking was carried out by the dropwise addition of the TEOS solution into the above solution. The stirring was continued at 100°C for 4 h to obtain the gel. The formed gel was cast on a glass petri dish, dried completely. The obtained membranes were washed with distilled water and dried at 37°C. The same process was used to prepare PVA/SP/Cu and PVA/SP/Ag nanocomposite membranes using Cu/SP and Ag/SP instead of pristine sepiolite. The different weight ratio of PVA and filler (sepiolite, Cu/SP, Ag/SP) and the codes used in this study are included in Table 2.1.

		Ρ\/Δ	Seniolite	Cu/SP	Aa/SP
Code	TEOS (%)	(wt. %)	(wt. %)	(wt. %)	(wt. %)
PVA/SP-1	10	90	10	-	
PVA/SP-2	20	90	10	-	
PVA/SP-3	10	70	30	-	
PVA/SP-4	10	70	30	-	
Cu/SP@PVA-1	10	90	-	10	
Cu/SP@PVA-2	20	90	-	10	
Cu/SP@PVA-3	10	70	-	30	
Cu/SP@PVA-4	20	70	-	30	
Ag/SP@PVA-1	10	90	-	-	10
Ag/SP@PVA-2	20	90	-	-	10
Ag/SP@PVA-3	10	70	-	-	30
Ag/SP@PVA-4	20	70	-	-	30

 Table 2.1:
 Identification
 codes
 and
 composition
 of
 different
 nanocomposite

 membranes.
 membranes.
 membranes
 membranes

2.6 Characterization Studies

2.6.1 Morphological analysis

The morphologies of nanocomposite membranes were evaluated by scanning electron microscope (SEM) (VEGA3 TESCAN). The samples were coated with gold (Au) to make them conductive before analysis.

2.6.2 Energy-dispersive X-ray spectrometry (EDS) analysis

The elemental composition of nanocomposite membranes was carried out by SEM (VEGA3 TESCAN.

2.6.3 Fourier transform infrared (FTIR) spectroscopy

The nanocomposite membranes were scanned from 4000-400 cm⁻¹ using an attenuated total reflectance mode at 100 scans and a resolution of 4 cm⁻¹.

2.6.4 Wide-angle X-ray diffraction (WAXD) analysis

The X-ray diffractometer (X'Pert Pro PANalytical) was used to evaluate the crystal structure of nanocomposite membranes between 20 to 45°. The equipment uses CuK α radiation (λ =1.54 Å) at a scanning rate of 0.5 degrees/sec, current of 36 mA, and voltage of 36 kV.

2.6.5 Mechanical properties

The mechanical features (modulus of elasticity and tensile strength) of the pure PVA and nanocomposite membranes were evaluated using a tensile testing machine SANS per ASTMD638-02 type V at a 1 mm/min.

2.7 Adsorption Studies

A stock solution of 1000 ppm of Cr (VI) was prepared by dissolving K₂Cr₂O₇ in deionized water (stakpure, Germany), and this stock solution was further diluted to obtain the desired dilution. The pH of the solution was adjusted to 7, using 0.1 N NaOH or 0.1 N HCl. The adsorption studies of nanocomposite membranes were carried out in batch mode at 37°C and 150 rpm in a shaking incubator (JSR, Korea). Effect of pH on the adsorption of Cr (VI) was monitored by varying pH (2-4) of Cr (VI) solution (60 ppm/10 mL) using 0.05 g/mL of nanocomposite membranes at 37°C for 6 h. The effect of the different initial concentrations of chromium Cr (VI) (2, 10, 20, 40, 60, 80, and 100 ppm/10 mL) on the adsorption capacity of nanocomposite membranes (0.05 g/mL) was determined at 37°C for 6 h. Optimum adsorption time of Cr (VI) solution (60 ppm/10 mL) by 0.05 g/mL of nanocomposite membranes was checked at an optimized pH and 37 °C for the different periods (10, 20, 30, 40, 50 and 60 min). Adsorption experiments were also done with different dosages (0.01, 0.5, 0.1 g/L) of the nanocomposite membrane. The concentration of adsorbed chromium was evaluated by atomic absorption spectroscopy (Shimadzu Atomic Adsorption/Flame Emission AA660). The adsorption capacity of chromium ions (Q) (mg/g) and chromium removal (R) (%) by nanocomposite membrane were evaluated by using Eq. 1 and 2 given below;

Q (mg/g) =
$$\frac{(C_0 - C_1) V_S}{W_m}$$
 (Eq. 1)

R (%) =
$$\frac{(C_0 - C_1)}{C_0} x \, 100$$
 (Eq. 2)

where C_o is an initial concentration (mg/L) of the chromium solution before the adsorption, C_1 is the final chromium concentration (mg/L) after adsorption, V_s is the volume of solution (L), and W_m is the weight (g) of the membrane.

2.8 Membrane Regeneration Studies

The effect of different desorbing agents (0.1M HCl, 0.1M NaOH, and deionized water) was studied to monitor the removal of adsorbed Cr (VI) from nanocomposite membranes. A piece of chromium loaded nanocomposite membranes was placed in an appropriate amount of desorption agent at 37°C and agitated at 150 rpm for 60 min.

The membranes were washed with deionized water, and the adsorption/desorption process was repeated for five cycles. The following formula was used for determining the desorption (%).

Desorption (%) = $\frac{Desorbed Cr (VI)}{Adsorbed Cr (VI)} \times 100$ (Eq 3)

2.9 Metal Nanoparticles Release Studies

The release of Ag and Cu NPs from the nanocomposite membranes was performed using inductively coupled plasma optical emission spectrometry (ICP-OES) analysis, as described by Zhao *et al.* (2017). A batch test was carried out by immersing a piece (2×4 cm²) of nanocomposite membranes in 40 mL of deionized water (pH=7.5). Tubes were then placed in a shaking incubator at 37°C and 150 rpm for 24 h. Subsequently, amounts of dissolved Ag and Cu ions were measured via ICP-OES. Two replicates of each experiment were carried out.

2.10 Antimicrobial Assays

Broth dilution assay was performed using four bacterial strains *Staphylococcus aureus* ATCC 25923, *Bacillus cereus* FA11 JN593008, *Escherichia coli* ATCC11775, and *Pseudomonas aeruginosa* ATCC 27853 to evaluate the antimicrobial potential of nanocomposite membranes. *S. aureus* and *E. coli* bacterial strains were used as per the ISO 22196 to monitor the antibacterial activity of the nanocomposite membrane. While the foodborne poisoning is due to the presence of *B. cereus* in the drinking water (Messelhäusser et al., 2014), *P. aeruginosa* is a common source of biofilm formation in the water supply (Gawish et al., 2019).

The antimicrobial assay of nanocomposite membranes was done (Díez et al., 2017). Bacterial cultures were refreshed in sterilized nutrient broth. The pH of nutrient broth was adjusted to 7 with the aid of 1 M sodium hydroxide (NaOH) solution before sterilization. The flask was inoculated with a single colony of the bacterial strain, and the flask was placed in a shaking incubator for 18 h at 150 rpm and 37°C. After 18 h of incubation, bacterial growth was measured via optical density (OD) at 600 nm, and optical density of inoculum was adjusted to 0.5 MacFarland (1.5×10⁸ cells per mL) and was further diluted by 1:150 to obtain 1×10⁶ cells per mL, using sterilized PBS to make a simulated wastewater sample. The antimicrobial assay was conducted against Cu/ SP @PVA-1, Cu/SP @PVA-3, Ag/SP @PVA-1, and Ag/SP @PVA-3 nanocomposite membranes. A piece (0.5×0.5 cm²) of the nanocomposite membrane was immersed in a test tube containing sterilized nutrient broth and inoculum. The test tubes were incubated for 18 h at 37°C and 150 rpm. After incubation, the viable bacterial cells were measured both in medium and attached to the membrane. Membranes were taken out and transferred to another set of sterilized test tubes containing 1 mL of fresh PBS.

The test tubes were placed in a shaker for 25-30 min. About 10-fold serial dilution was made separately both from medium and membrane washing. The CFU/ mL was counted using agar spotting method (Thomas et al., 2015). The sectors were made on the reverse side of the Petri plate containing sterilized nutrient agar, and a 2 μ L sample was spotted in each sector. Plates were then allowed to dry for 10-15 min and were incubated at 37°C for 16 h. The acceptable number of colonies in each sector were ranging from 6-60. The antimicrobial assay was repeated for five cycles. The nanocomposite membranes were recovered, washed with sterilized distilled water, and dried at 37°C. The surface morphologies of the nanocomposite membranes were examined by scanning electron microscopy after gold coating to visualize the attachment of bacterial cells. The antimicrobial assays were carried out in duplicates. Results are presented as mean with standard deviation. The means were further analyzed by ANOVA and least significant difference, LSD at 0.05 probability.

3. RESULTS AND DISCUSSION

3.1 Preparation of Cu/SP and Ag/SP

3.1.1 Scheme of reaction

The scheme of synthesis of Cu/SP containing Cu_2O , CuO, Cu nanoparticles, and Ag/SP containing Ag_2O , AgO and Ag nanoparticles is shown in Fig. 3.1. The growth of metal nanoparticles on the SP might undergo selective adsorption, reduction, nucleation, and growth process (Xu et al., 2005; Siddiqui *et al.*, 2013; Goudarzi et al., 2016).





3.2 Characterization Studies of Cu/SP and Ag/SP

3.2.1 Color change

Fig. 3.2 (a-b) shows the change in the color of pristine sepiolite after synthesis of Cu/ SP and Ag/SP. The color of the Cu/SP turned into brick red from whitish, while the Ag/ SP was greenish after the formation of Ag nanoparticles.

3.2.2 Particle size and zeta size analysis

Table 3.1 shows the yield, particle size, polydispersity index, and zeta potential of Cu/SP and Ag/SP. The diameters of Cu/SP and Ag/SP were 286 and 183 nm, respectively. While, the polydispersity values for Cu/SP and Ag/SP were 0.42 and 0.50, respectively. The zeta potential of pristine sepiolite was -16.1 mV, while the zeta potential values of Cu/SP and Ag/SP were -12.8 and -19.3 mV, respectively. The negatively charged surface of Cu/SP and Ag/SP nanoparticles was mostly due to the OH⁻ groups contributed by sepiolite. A higher value of zeta potential observed in the



Fig. 3.2: Pictorial view of sepiolite; (a) Cu/SP; and (b) Ag/SP

case of Ag/SP indicated its better electrostatic stability in comparison to Cu/SP. The electrostatic stability of silver nanoparticles was increased from – 5.9 mV to -41 mV in Ag/graphene oxide nanocomposite (Jaworski et al., 2018).

Table 3.1:	Yield, particle size, polydispersity index, and zeta potential of Cu/SP and	b
	Ag/SP.	

Sample code	Yield (%)	Particle size (nm)	Polydispersity index (PDI)	Zeta potential (mV)
SP	N.D.	180±1.12	0.924±1.23	-16.1±2.11
Cu/SP	65.23±2.67	245±1.50	0.424±1.45	-12.8±3.10
Ag/SP	75.23±2.15	183±2.50	0.501±1.98	-19.3 ±6.17

3.2.3 EDS analysis

Fig. 3.3 (a-b) and 3.4 (a-d) show the EDS analysis of pristine sepiolite, Cu/SP, and Ag/SP. The EDS spectrum of pristine sepiolite showed the presence of Si, O, and Mg atoms, which are the main components of sepiolite (Fig. 3.3 a-b). Moreover, the presence of Cu atoms confirmed the incorporation of Cu nanoparticles in the Cu/SP (Fig. 3.4 a-b). Also, the observation of Ag atoms was attributed due to the addition of Ag into Ag/SP (Fig. 3.4 c-d). The quantity of Mg atom in sepiolite remained the same after modification with Cu and Ag; therefore, it is believed that no leaching of Mg occurred during the deposition of metal nanoparticle on the surface of sepiolite fibers (Fig. 3.4 a-d). An absence of Mg in the EDS analysis of acid-activated sepiolite was found due to the complete leaching of Mg during the formation of silica nanotubes (Yao et al., 2019).



(b)

(d)



Fig. 3.3: EDS analysis of pristine sepiolite (a-b).









Fig. 3.4: EDS analysis of Cu/SP (a-b); and Ag/SP (c-d).

3.2.4 SEM analysis

The SEM images of pristine sepiolite, Cu/SP, and Ag/SP are depicted in Fig. 3.5 (a-c). The SEM image of pristine sepiolite demonstrated bundled needle-like morphology (Fig. 3.5 a), as reported previously (Shakil et al., 2017). The morphology of pristine sepiolite remained intact after the incorporation of Cu and Ag nanoparticles in the resulting Cu/SP and Ag/SP (Fig. 3.5 b-c). However, spherical nanoparticles on the surface of sepiolite fibers were also seen. Similarly, the addition of palladium nanoparticles did not change the morphology of sepiolite fibers (Sadjadi et al., 2018).



Fig. 3.5: Scanning electron micrographs of pristine sepiolite (a); Cu/SP (b); and Ag/SP (c) (arrows indicated the presence of metal particles on the sepiolite fibers).

3.2.5 TEM analysis

TEM of Cu/SP and Ag/SP is given in Fig. 3.6 (a-b). The copper nanoparticles were embedded in the sepiolite fibers as expected in the case of Cu/SP. Similarly, the deposition of silver nanoparticles was evident on sepiolite nanofiber. Metal nanoparticles were well dispersed on sepiolite fiber. Additionally, no free agglomerates of metal nanoparticle were observed in transmission electron micrographs of Cu/SP and Ag/SP. The agglomerates of silver nanoparticles were also found in the scanning



Fig. 3.6: Transmission electron micrographs of Cu/SP (a) and Ag/SP (b) (arrows indicated the metal nanoparticle deposition the sepiolite fibers).

electron micrographs of silver containing sepiolite. Previously, it was reported that free high surface energy of the synthesis system led to their agglomeration of metal nanoparticles (Raffi et al., 2010).

3.2.6 FTIR analysis

Fig. 3.7 and 3.8 (a-b) show the FTIR spectra of pristine sepiolite, Cu/SP, and Ag/ SP. The FTIR spectrum of pristine sepiolite showed three smaller absorption bands at 3568, 3667, and 3691 cm⁻¹, which are corresponding to bounded water molecules and structural OH group stretching and a wide broad absorption band at 3420 cm⁻ ¹ (zeolitic water molecules) (Jia et al., 2004). Thus, there is complete coverage of adsorbed and zeolitic water molecules on the surface of sepiolite nanofibers. Other absorption bands were found at 1660 cm⁻¹ (vibrations of zeolitic water molecules), 1653 cm⁻¹ (vibrations of bounded water molecules), 1210 and 1080 cm⁻¹ (a shoulder of Si-O group), 1021 and 474 cm⁻¹ (Si-O-Si), 977 cm⁻¹, (Si-O bond stretching), 690 and 645 cm⁻¹ (Mg-O) (Myriam et al., 1998; Jia et al., 2004). While the Si-O-Mg (440 cm⁻¹) and Mg–O (690 and 637 cm⁻¹) vibrations were evident in the FTIR spectrum of pristine sepiolite (Myriam et al., 1998). A new absorption band appeared at 535 cm^{-1,} which was due to metal-oxygen (Cu–O) bond, while the absorption band at 876 cm⁻¹ was due to Cu–O–H bonds (Aguirre et al., 2011). Two new narrow bonds were observed at 539 and 422 cm⁻¹ due to stretching vibrations of Cu-O bond in the FTIR spectrum of CuO nanoparticle (Xu et al., 2005). An absorption band found at 550 cm⁻¹ in the FTIR spectrum of Ag/SP was ascribed to silver oxide, as reported earlier (Siddiqui et al., 2013). In another study, the absorption band at 540 cm⁻¹ was corresponding to the Ag-O bond in the FTIR spectrum of Ag nanoparticles (Goudarzi et al., 2016). A considerable decrease in the intensities of absorption bands in a region at 3400-3700 cm⁻¹ was observed. This behavior was due to ionic interactions of coordination water molecules (bounded to Mg²⁺ ions found at the corner of octahedral sheets) and zeolitic water molecules (water molecules bonded to Mg²⁺ ions via hydrogen bonding) of sepiolite with CuO, Cu, AgO and Ag nanoparticles in FTIR spectra of Cu/SP and Ag/ SP. The magnetite and anatase NPs attached to sepiolite via Si-O-M links during the in situ formation of metal (M)-oxide NPs on the sepiolite fibers (Aranda et al., 2008; González-Alfaro et al., 2011; Akkari et al., 2017). The intensities of other characteristic absorption bands found at 1662, 1213, 1089, 1016, 976, and 792 cm⁻¹ were sharply declined.



Fig. 3.7: FTIR spectra of sepiolite and Cu/SP in the range of 4000-400 cm⁻¹ (a) and magnified region of 2000-400 cm⁻¹ (b).



Fig. 3.8: FTIR spectra of sepiolite and Ag/SP in the range of 4000-400 cm⁻¹ (a) and magnified region of 2000-400 cm⁻¹ (b).

3.2.7 WAXD analysis

The WAXD diffractogram of the pristine sepiolite, Cu/SP, and Ag/SP are shown in Fig. 3.9 (a-b). The diffraction pattern of pristine sepiolite showed a characteristic reflection at 7.3° (110) with a d-value of 16.87 nm. Other characteristic reflections of pristine sepiolite were found at 13.4° (040), 20.45° (131), 23.69° (260), and 26.5° (080). The corresponding interplanar distances were 11.30, 27.37, 17.20, and 34.58 nm, respectively. The characteristic reflections of sepiolite were found at 7.6° (110), 13.2° (040), 19.7 ° (031), 20.6° (131), 23.7°(260) and 26.6°(080) (Tartaglione et al., 2008; Shakil et al., 2017). The diffraction pattern of Cu/SP showed a significant decrease in intensities of all characteristic reflections of sepiolite. This behavior was due to the modification of Si-OH groups present on the external surface of sepiolite with Cu₂O and CuO nanoparticles. Moreover, three new reflections appeared at 34.91, 39.82, and 43.2° corresponding to (111), (200) and (111) diffraction planes of Cu, CuO and Cu₂O nanoparticles in diffractogram of Cu/SP, respectively. The reflections at 34.91° (111), 39.82° (200), 43.2° (111), 50.3° (200) and 73.9° (220) corresponded to the characteristic face-centered cubic (FCC) crystals of Cu, CuO and Cu₂O nanoparticles, respectively (Raffi et al., 2010; Mikami et al., 2019). Similarly, a prominent decrease in the characteristic reflections of sepiolite was observed in the diffractogram of Ag/SP. Additionally, the characteristic reflections of Ag, Ag, O, and Ag/Ag, O nanoparticles were observed at 26.7, 38.2, and 44.5° in the diffractogram of Ag/SP due to modification of sepiolite surface with silver nanoparticles as reported earlier (Dorobantu et al., 2015). The XRD diffractogram of Ag₂O nanoparticles demonstrated characteristic reflections at 27.94 and 32.27, which corresponded to (110) and (111) lattice planes of facecentered-cubic silver crystals (Dhoondia and Chakraborty, 2012; Kumar et al., 2015a). Moreover, the presence of the characteristic reflections, i.e., 7.6° (110), 23.7° (260) and 26.6° (080) of sepiolite in the diffractograms of Ag/SP and Cu/SP confirmed that the native fibrous structure of sepiolite had not disrupted due to formation of metal nanoparticles over them. Table 3.3 shows the comparison of peak position and crystallite size of sepiolite, Cu/SP, and Ag/SP. The sizes of crystallite at (110) and (260) lattice planes of pristine sepiolite were found to be 16.87 and 17.20 nm, respectively. While the sizes of these crystallites were increased to 22.51 and 20.64 nm in the case of Cu/SP. The sizes of crystallites at (110) and (260) lattice planes were 20.24 and 17.31 nm upon the functionalization of sepiolite with silver nanoparticles (Table 3.3).



Fig. 3.9: WAXD diffractograms of sepiolite; Cu/SP (a); and Ag/SP (b) nanohybrids in a range of 5-45 °.

Sample	Lattice plane	20	Size (nm)
	(110)	7.03	16.87
	(40)	13.4	11.30
Pristine Sepiolite	(131)	20.45	27.37
	(260)	23.69	17.20
	(80)	26.54	34.58
	(110) SP	7.42	20.42
	(40) SP	13.32	13.32
	(260) SP	28.32	23.82
Ag/SP	(110) Ag ₂ O	26.83	17.31
	(111) Ag ₂ O	38.21	26.72
	(200) Ag ₂ O/Ag	44.50	14.52
	(110) SP	7.35	22.51
	(131) SP	20.54	25.66
	(260) SP	23.62	20.64
	(080) SP	26.61	23.41
Cu/SP	(111) Cu ₂ O, (002) CuO	34.91	8.82
	(200) Cu ₂ O, (111) CuO	39.82	17.90
	(111) Cu	43.29	44.55

Table 3.3.A comparison of peak position and crystallite size of sepiolite, Cu/SP, and
Ag/SP.

3.2.8 Antimicrobial activity

Fig. 3.10 (a-b) shows the antimicrobial properties of different concentrations of Cu/SP and Ag/SP against *Escherichia coli* ATCC11775 and *Pseudomonas aeruginosa* ATCC 27853. No bacterial growth was observed against the different tested concentrations of Cu/SP and Ag/SP (Fig. 3.11). The release of silver and copper metal ions was responsible for the killing of microbial cells. Metal oxide nanoparticles have biocidal properties, and they can efficiently target the bacterial population. Therefore, they are commonly used to design the antibacterial nanocomposite membranes with a noteworthy reduction in biofouling. Previously, it was reported that the Ag₂O (Kumar et al., 2015b), ZnO (Wang et al., 2018), CuO (Raffi et al., 2010), and TiO₂ (Sodagar et al., 2017) nanoparticles showed good antimicrobial properties.



Fig. 3.10: Effect of different concentrations of Cu/SP (a) and Ag/SP (b) on the growth of bacterial strains.

3.3 **Preparation of Nanocomposite Membranes (PNCMs)**

Phase inversion method was used to prepare PVA/SP, Cu/SP@PVA, and Ag/SP@ PVA nanocomposite membranes (Fig. 3.12). The choice of the composition of polymer solutions, solvent, non-solvent, film casting conditions, and coagulation bath composition are the key parameters for membrane preparation. However, this method offers the advantage of large morphological variations by varying mentioned process parameters.



Fig. 3.11: Antibacterial activity of Cu/SP and Ag/SP at different concentrations; (a) 10 mg, (b) 7.5 mg, (c) 5 mg, (d) 4 mg, (e) 3 mg, (f) 2 mg, (g) 1 mg.





Fig. 3.12: Mechanism of preparation of multifunctional nanocomposite membrane (a); photographs of PVA/SP (b), Cu/SP@PVA(c) and Ag/SP@PVA (d) nanocomposite membranes.

3.4 Characterization of Nanocomposite Membranes

3.4.1 SEM and EDS analysis

Fig. 3.13 (a-b) shows the SEM of PVA/SP nanocomposite membranes. The sepiolite exhibited fibrous morphology. These fibers were well dispersed and embedded into a polymeric matrix in the scanning electron micrograph of the PVA/SP nanocomposite membrane. On the other hand, well-dispersed metal nanoparticles loaded sepiolite fibers were evident in the scanning electron micrographs of Cu/SP@PVA and Ag/SP@PVA nanocomposite membranes (Fig. 3.14 a-b and 3.15 a-b). The mechanical, chemical and thermal treatments during the preparation of Cu/SP and Ag/SP caused the breakdown of sepiolite bundles into individual fibers. Moreover, the silver nanoparticles and copper nanoparticle containing sepiolite fibers and polymeric matrix were crosslinked as a result of interactions between the crosslinking agents and polymer. The intermolecular crosslinking of the PVA chains through TEOS resulted in



Fig. 3.13: Scanning electron micrographs (a-b) and elemental dispersive spectroscopy analysis (c-d) of PVA/SP nanocomposite membranes.



Fig. 3.14: Scanning electron micrographs (a-b) and elemental dispersive spectroscopy analysis (c-d) of Cu/SP@PVA-3 nanocomposite membranes.

the formation of a three-dimensional network structure, which is mainly responsible for the formation of crosslinked polymer nanocomposite membranes. EDS analysis of PVA/SP, Cu/SP@PVA, and Ag/SP@PVA nanocomposite membrane indicated the presence of C, O, Mg, Si, Cu, and Ag atoms (Fig. 13-15 c-d).



Fig. 3.15: Scanning electron micrographs (a-b) and elemental dispersive spectroscopy analysis (c-d) of Ag/SP@PVA nanocomposite membranes.

3.4.2 FTIR analysis

Fig. 3.16 (a-b) shows the FTIR spectra of PVA, sepiolite, and TEOS. The IR spectrum of PVA demonstrated a broad absorption band between 3500 to 3250 cm⁻¹, corresponding to OH stretching vibration of intermolecular and intramolecular hydrogen bonding. While the C-H stretching vibration of an alkyl group is evident in the region from 3000 to 2840 cm⁻¹. The absorption band at 1730 cm⁻¹ was ascribed to the C-O stretching vibration of the residual acetate group from PVA (Costa-Júnior et al., 2009; Islam et al., 2015). The IR spectrum of TEOS showed characteristic absorption bands at 2975 cm⁻¹ (asym. C-H stretching), 2930 cm⁻¹ (asym. C-H stretching), 2892 cm⁻¹ (asym. C-H stretching), 1168, 960 cm⁻¹ (CH rocking) and 793 cm⁻¹ (SiO, asym) (Rubio et al., 1998).

The FTIR spectra of the PVA/SP nanocomposite membrane are given in Fig. 3.17 (a-b). The FTIR spectrum of the PVA/SP-1 nanocomposite membrane showed a significant decrease in the intensity of the broad absorption band in a region 3570 to 2985 cm⁻¹, which indicated that the silanol (Si-OH) groups of sepiolite reacted with OH groups of PVA during crosslinking reactions. These results are consistent with the previous finding (Jiang et al., 2018). According to them, the FTIR spectrum of silica/ montmorillonite (MMT) nanocomposites demonstrated a significant reduction of the intensity of absorption bands due to condensation reactions that occurred between -OH groups present on the silica with the OH groups on the MMT surface. The absorption band at 2945 and 1730 cm⁻¹ was indicating the presence of $-CH_3$ and C=O groups,



Fig. 3.16: FTIR spectra of PVA, TEOS, and pristine sepiolite in the range of 4000-400 cm⁻¹ (a) and magnified region of 2000-400 cm⁻¹ (b).



Fig. 3.17: FTIR spectra of PVA/SP nanocomposite membranes in the range of 4000-400 cm⁻¹ and magnified region of 2000-400 cm⁻¹ (b).

respectively, in the FTIR spectrum of PVA/SP-1 nanocomposite membrane, as reported earlier in case of PVA/SP nanocomposites (Alkan and Benlikava, 2009). The formation of siloxane bonds was evident due to the presence of an absorption band at 1080 cm⁻¹ in the IR spectrum of the PVA/SP-1 nanocomposite membrane. On the other hand, the increase in the quantity of TEOS in the PVA/SP-2 nanocomposite membrane gave a broad absorption band in a region from 3570 to 2985 cm⁻¹ due to the formation of intermolecular and intramolecular hydrogen bonds contributed by TEOS. Similarly, the absorption bands due to siloxane bond formation were observed at 1145 and 1020 cm⁻ ¹, which were ascribed to Si–O–Si and Si–O–C functional groups (Velasco-Santos et al., 2011). Additionally, the presence of unreacted TEOS was evident by an absorption band at 830 cm⁻¹ in the IR spectrum of the PVA/SP-2 nanocomposite membrane. In another study, the unreacted silane demonstrated an absorption band at 817 cm⁻¹ in the FTIR spectrum of multiwalled carbon nanotube/vinyl ester polymer composites (Avilés et al., 2013). On the other hand, the FTIR spectrum of the PVA/SP-3 nanocomposite membrane indicated an increase in the intensity of OH stretching vibrations in a region at 3570 to 2985 cm⁻¹ due to an increase in the amount of sepiolite. While the absorption band at 980 cm⁻¹ (CH rocking vibrations) was indicating the successful grafting of TEOS on sepiolite in the IR spectrum of the PVA/SP-3 nanocomposite membrane. The siloxane linkages were developed between polymer matrix and sepiolite due to the action of TEOS, as evident by the absorption band at 1080 cm⁻¹. These siloxane linkages provide stability to nanocomposite membranes in the aqueous environment. The intensity of the absorption band due to the presence of unreacted silane at 830 cm⁻¹ was also declined. On the other hand, a maximum degree of crosslinking was observed in the case of the PVA/SP-4 nanocomposite membrane. The FTIR spectra of poly(vinyl alcohol)-polysulfone composite membranes demonstrated a decrease in intensities of absorption bands in region at 3000-3600 cm⁻¹ (OH stretching vibrations), 1630-1760 cm⁻¹ (-C=O- groups in -C=O-O-C- groups), 1300 cm⁻¹ (stretch of -C-Ogroup in -C=O-O-H groups) with an increase in degree of crosslinking induced by crosslinking agent (Peng et al., 2011).

Fig. 3.18 (a-b) shows the FTIR spectra of Cu/SP@PVA nanocomposite membranes. The FTIR spectra of Cu/SP@PVA nanocomposite membranes demonstrated a sharp decrease in the intensities of absorption bands in the region from 3570-2900 cm⁻¹ as a result of the crosslinking effect induced by TEOS. The formation of siloxane linkages was evident by the broadening of absorption bands in the region from 1000-1100 cm⁻¹. There was a formation of a coordinated bond between O atom of OH groups from PVA and Cu²⁺ ion of copper-containing sepiolite (Cu/SP). The oxygen atom of OH groups of PVA contributed lone pair of electrons to TIO⁴⁺ resulted in the self-assembly of TIO₂ nanoparticles on the PVA/PES composite membrane (Pourjafar et al., 2012).



Fig. 3.18: FTIR spectra of Cu/SP@PVA nanocomposite membranes in the range of 4000-400 cm⁻¹ (a) and magnified region of 2000-400 cm⁻¹ (b).

The FTIR spectra of Ag/SP@PVA nanocomposite membranes are given in Fig. 3.19 (a-b). The OH stretching vibrations (3000-3600 cm⁻¹), -C=O- stretching vibration (1730 cm⁻¹), -C-O- stretching (1330 cm⁻¹) were significantly declined due to crosslinking of Ag/



Fig. 3.19: FTIR spectra of Ag/SP@PVA nanocomposite membranes in the range of 4000-400 cm⁻¹ (a) and magnified region of 2000-400 cm⁻¹ (b).

SP@PVA nanocomposite membranes. The OH bending vibrations of adsorbed water molecules at 1638 cm⁻¹ on MMT was sharply declined in silver organic montmorillonite Ag-OMMT nanocomposite (Zhang et al., 2018). In this study, a coordinate bond formation was responsible for linking the polymer matrix and Ag+ ions of Ag/SP in Ag/ SP@PVA nanocomposite membranes.

An absorption band at 1560 cm⁻¹ was demonstrating the presence of nitro compound (N-O) due to the presence of precursor salts, i.e., $AgNO_3$ and Cu $(NO_3)_2$ in IR spectra of both Ag/SP@PVA-2 and Cu/SP@PVA-2 nanocomposite membranes. The shift in intensities of absorption bands from 3421 and 1652 cm⁻¹ to 3441 and 1633 cm⁻¹ was reported as a result of van der Waals interactions between the hydroxyl groups of the zeolite and the positive charge on the surface of silver ions (Shameli et al., 2010).

3.4.3 WAXD analysis

The WAXD diffractograms of pristine sepiolite, PVA/SP-1, and PVA-SP-3 nanocomposite membranes are shown in Fig. 3.20. The PVA/SP nanocomposite membranes showed a prominent decrease in the intensities of all characteristic reflections of sepiolite due to a uniform dispersion of sepiolite fibers in the PVA matrix. The low-intensity of the diffraction peak at 2θ =7.30° (110) in sepiolite/polyurethane nanocomposites is ascribed to the complete exfoliation of sepiolite bundles into sepiolite fibers within



Fig. 3.20: WAXD diffractograms of pristine sepiolite, PVA/SP-1, and PVA-SP3 nanocomposite membranes in a range of 5-45 °.

polymer matrix (Chen et al., 2007). Similarly, a significant decrease in the relative intensities of all characteristic reflections was observed in the WAXD diffractogram of Cu/SP@PVA-3 and Ag/SP@PVA-3 nanocomposite membranes (Fig. 3.21 a-b). The presence of the characteristic reflection of sepiolite in all samples confirmed that sepiolite had maintained its structural integrity upon the crosslinking reactions of metal nanoparticles containing sepiolite with PVA (Alkan and Benlikaya, 2009).



Fig. 3.21: WAXD diffractograms of PVA/SP-3, Cu/SP@PVA-3 (a); and Ag/SP@PVA-3 (b) nanocomposite membranes in a range of 5-45 °.

3.4.5 Mechanical properties

Mechanical properties of nanocomposite membranes are dependent upon the quantity of nanofiller and crosslinker used during the preparation of nanocomposite membranes. An overview of the mechanical properties of nanocomposite membranes is given in Table 3.4. It was found that the values of modulus of elasticity and tensile strength of PVA were significantly increased in the resulting PVA/SP nanocomposites. The values of mechanical strength and elongation of break of polysulfone/sepiolite nanocomposite were slightly enhanced due to an increase in the quantity of sepiolite (Khodami et al., 2019). An increasing amount of sepiolite containing metal loaded nanoparticles led to an increase in the mechanical properties of resulting polymer nanocomposite membranes. An increase in the value of tensile strength and modulus of elasticity was observed for SP@PVA-3, Ag/SP@PVA-3, and Cu/SP@PVA-3 nanocomposite membranes. This behavior was due to good dispersion of pristine sepiolite and metal nanoparticle loaded sepiolite nanofibers so that anisotropic needle-like shape of the sepiolite fibers and crosslinked network structure enhanced the mechanical properties. On the other hand, the high quantity of TEOS led to the brittleness of polymer nanocomposite membranes and ultimately decreased the values of modulus of elasticity and tensile strength, as observed in the case of PVA/SP-4, Cu/SP@PVA-4, and Ag/SP@PVA-4 nanocomposite membranes.

Sample	Modulus of elasticity (MPa)	Tensile strength (MPa)
PVA	1.56 ± 0.25	3.72 ± 0.21
PVA/SP-1	2.03 ± 0.14	3.58 ± 0.21
PVA/SP-2	1.85±0.15	6.58±1.21
PVA/SP-3	5.95±1.25	58.20 ± 0.48
PVA/SP-4	12.78 ± 0.42	37.80 ± 0.45
Cu/SP@PVA-1	5.05 ± 0.18	4.80 ± 0.46
Cu/SP@PVA-2	5.58±1.45	6.35±0.12
Cu/SP@PVA-3	6.50±0.35	59.95±0.87
Cu/SP@PVA-4	4.50±0.89	37.32±1.12
Ag/SP@PVA-1	7.50±0.90	4.15±0.75
Ag/SP@PVA-2	5.56 ± 0.32	6.80 ± 0.82
Ag/SP@PVA-3	6.26 ± 0.15	58.56±0.23
Ag/SP@PVA-4	6.58 ± 0.33	35.52 ± 0.53

Table 3.4: An overview of the mechanical properties of nanocomposite membranes.

3.5 Release Studies of Metal Nanoparticles

The PVA/SP-1, PVA/SP-3, Cu/SP@PVA-1, Cu/SP@PVA-3, Ag/SP@PVA-1, and Ag/ SP@PVA-3 nanocomposite membranes were selected for release studies of metal nanoparticles due to their superior mechanical properties. A batch test was performed to evaluate the stability of Ag and Cu nanoparticles in the polymer nanocomposite membrane. The release of metal ions from Ag/SP@PVA-1, Ag/SP@PVA-3, Cu/SP@ PVA-1, and Cu/SP@PVA-3 nanocomposite membranes is shown in Fig. 3.22. The amount of Ag⁺ ions released from Ag/SP@PVA-1 and Ag/SP@PVA-3 nanocomposite membranes immersed in deionized water at pH 7.5 after 24 h were 11.5 and 4.25 µg/L, respectively. The release of Cu²⁺ ions from Cu/SP@PVA-1 and Cu/SP@PVA-3 nanocomposite membranes into deionized water at pH 7.5 was 16.62 and 18.03 µg/L, respectively. The rate of release of copper was higher than that of silver because copper was already in the Cu(II) oxidation state in the sepiolite material, whereas silver required an additional oxidation step from Ag(0) to Ag⁺, as reported earlier in case of polysulfone-polyvinylpyrrolidone/sepiolite/Cu nanocomposite membranes. This release of metal ions in the treated water is a big challenge in the use of polymer nanocomposite membranes for the removal of heavy metals from wastewater. Therefore, it requires to control the leaching out of metal ions from the membrane and make it more stable for potential wastewater treatment purpose. There is a need to introduce the covalent bonding between the polymer and nanoparticles to improve the stability of nanocomposite membranes.



Fig. 3.22: The release of metal ions from Ag/SP@PVA-1, Ag/SP@PVA-3 (a); Cu/SP@ PVA-1 and Cu/SP@PVA-3 (b) nanocomposite membranes.

3.6 Adsorption Studies

3.6.1 Effect of initial pH

The adsorption properties are strongly dependent on the initial pH of the solution because it affects both the availability of metal ions in the solution as well as the vacant sites of the adsorbent materials. Therefore, the initial pH is optimized to obtain the maximum removal percentage of chromium ions using 0.05 g of nanocomposite membrane. The contact time was 6 h, and the temperature was maintained at 37 °C. The concentration of the stock solution was kept at 60 mg/mL. Fig. 3.23 (a-f) shows the effect of pH on adsorption capacity (mg/g) and chromium removal (%) of PVA/SP-1, PVA/SP-3, Cu/SP@PVA-1, Cu/SP@PVA-3, Ag/SP@PVA-1, and Ag/SP@ PVA-3 nanocomposite membranes. Chromium ions are present in different forms at different values of pH. The Cr⁺⁶ ion exists as dichromate (Cr₂O₇²⁻) at pH below 4, as hydrochromate (HCrO₄⁻) and dichromate (Cr₂O₇²⁻) at 4–8 pH value, and as chromate (CrO²⁻) at pH above 8 (Zhang et al., 2010; Samani and Toghraie, 2019). Typically, the charge of the surface of the adsorbent played a key role in the adsorption process (Yu et al., 2014; Yu et al., 2015). The pH at the point of zero charges (pH pzc) for sepiolite is about 7.4 (Lazarević et al., 2007). Maximum adsorption capacity and chromium removal of PV A/SP-3, Ag/SP@PVA-3, and Cu/SP@PVA-3 nanocomposite membrane was observed at initial pH 4. This behavior was due to the presence of a higher quantity of sepiolite that indirectly provided a higher concentration of OH groups. The OH groups of nanocomposite membranes acted as vacant adsorption sites for Cr (VI) ions. These OH groups became positively charged at low pH value. The possible adsorption mechanism is the coulombic forces of attraction between the negatively charged HCrO₄⁻ and positively charged $-OH_2$ groups of sepiolite. Therefore, oxyanions of chromium are adsorbed on the positively charged adsorbent surface. The maximum removal of Cr (VI) was found at pH 7 by an aqueous solution of nanoalumina due to coulombic forces of attraction between negatively charged Cr ions and positively charged adsorbent surface (Zhang et al., 2010).

On the other hand, low chromium removal % was found at pH 2 in the case of PVA/ SP-1, PVA/SP-3, Cu/SP@PVA-1, Cu/SP@PVA-3, Ag/SP@PVA-1, and Ag/SP@ PVA-3 nanocomposite membranes due to repulsion between H⁺ ions and Cr⁺ ions. In another study, low uptake of Gd (III) by raw sepiolite was observed at low pH due to the protonation of binding sites of sepiolite, which indirectly inhibited the binding of heavy metals (Yao et al., 2019). Thus, the initial pH was kept at 4 for subsequent adsorption experiments using PVA/SP, Ag/SP@PVA, and Cu/SP@PVA nanocomposite membranes.



Fig. 3.23: Effect of initial pH on the adsorption of Cr (VI) using multifunctional nanocomposite membranes.

3.6.2 Effect of time

Fig. 3.24 (a-f) shows the effect of time on the adsorption of hexavalent chromium ions by the nanocomposite membranes. The effect of contact time was studied at pH 4 using 0.05 g of PVA/SP, Ag/SP@PVA, and Cu/SP@PVA nanocomposite membranes. The temperature was maintained at 37 °C, and initial chromium concentration was kept at 60 ppm. The optimal contact time for maximum Cr removal (%) was 10 min for PVA/SP-3, Ag/SP@PVA-3, and Cu/SP@PVA-3 nanocomposite membranes. This behavior was due to the availability of maximum vacant sites for adsorption of Cr (VI) during initial contact time. There was no significant increase in the adsorption capacity of the nanocomposite membrane after this time because there was a high competition between hexavalent chromium molecules for adsorption on the adsorbent surface. A similar pattern for the removal of chromium by nano-alumina adsorbents was observed (Paul et al., 2012).



Fig. 3.24: Effect of time on the adsorption of Cr (VI) using multifunctional nanocomposite membranes.

3.6.3 Effect of the initial chromium concentration

The effect of different initial chromium concentrations (2, 10, 20, 40, 60, 80, and 100 ppm) on the adsorption properties of nanocomposite membranes were studied, and the results are shown in Fig. 3.25 (a-f). This adsorption experiment was carried out with a 0.05 g adsorbent dose at 37 °C for 15 min. The Cr (VI) removal (%) was increased with an increase in the initial Cr (VI) concentration in PVA/SP-3, Ag/SP@



Fig. 3.25: Effect of initial concentration on the adsorption of Cr(VI) using multifunctional nanocomposite membranes.

PVA-3, and Cu/SP@PVA-3 nanocomposite membrane. This behavior was due to the synergistic effect of an increase in the number of vacant sites due to a high quantity of sepiolite in the nanocomposite membrane and the availability of more metal ions at higher concentration of the stock solution. The maximum adsorption capacity of PVA/SP-3, Ag/SP@PVA-3, and Cu/SP@PVA-3 nanocomposite membrane was observed when an initial chromium concentration was kept at 60 ppm, after which, the decline in adsorption capacity was observed. A high solute concentration gradient is responsible for controlling the mass-transfer resistance between solution and solid surface (Vinod et al., 2010). The decline in adsorption capacity of PVA/SP@PVA-3 nanocomposite membranes at higher initial chromium concentration were due to the complete occupation of vacant sites available for binding with Cr ions. The adsorption capacity of an aqueous solution of nano-alumina was increased up to 20 mg/mL of initial chromium concentration, followed by a decline at 100 mg/mL (Paul et al., 2012).

3.6.4 Effect of adsorbent

Fig. 3.26 (a-f) shows the influence of the quantity of adsorbent dose of PVA/SP-1, PVA/SP-3, Cu/SP@PVA-1, Cu/SP@PVA-3, Ag/SP@PVA-1, and Ag/SP@PVA-3 nanocomposite membranes on the Cr (VI) removal. These studies were carried out at an initial pH 4 in the case of PVA/SP, Ag/SP@PVA, and Cu/SP@PVA nanocomposite membranes. The initial concentration of chromium and temperature was kept at 60 ppm and 37°C, respectively. The maximum removal of chromium (%) was observed in the presence of 0.05 g of PVA/SP-3, Ag/SP@PVA-3, and Cu/SP@PVA-3 nanocomposite membranes. This behavior was due to an increasing number of vacant sites available on nanocomposite membranes for chromium removal. The Cu (II) removal (%) of chitosan/PVA beads crosslinked by TEOS was enhanced with an increase in the size of the adsorbent dose (Kamal et al., 2016). On the other hand, the adsorption capacity (mg/g) of nanocomposite membranes was declined with an increase in adsorbent dose.

3.6.5 Absorption studies under optimized conditions

Fig. 3.27 shows the comparison of adsorption capacities and chromium removal (%) of PVA/SP-3, Ag/SP@PVA-3, and Cu/SP@PVA-3 nanocomposite membranes under optimized conditions. The optimized condition (initial pH = 4; initial chromium ion concentration= 60 ppm; time = 10 min; adsorbent dose= 0.01 g; temperature = 37 °C) were used to execute this experiment. It was observed that the adsorption capacities (mg/g) and chromium removal (%) of all three systems were approximately similar. These results are in accordance with the hypothesis that the loading of metal nanoparticle did

not alter the adsorption potential of PVA/SP nanocomposite membranes. The metal nanoparticles were added to control the biofouling of the nanocomposite membrane.

The adsorption of chromium on the nanocomposite membrane occurred via electrostatic interactions (physical process). This process is a rapid one in comparison to chemical adsorption. Previously, the silica gel material modified with nitrilotriacetic acid demonstrated the removal of copper, cadmium, and lead ions via electrostatic



Fig. 3.26: Effect of adsorbent dose on the adsorption of Cr (VI) using multifunctional nanocomposite membranes.



Fig. 3.27: The comparison of adsorption capacities and chromium removal (%) of nanocomposite membranes

adsorption (Li et al., 2019). According to them, there is a diffusion of heavy metal ions from the external aqueous medium to the surface of the adsorbent, followed by internal diffusion to available sites on the adsorbent. Finally, the adsorption reaction occurred between functional groups on the available sites and heavy metal ions. The occurrence of physisorption is also reported between arsenic molecules and adsorbent surfaces, which did not alter the configuration of adsorbate and adsorbent (Siddiqui et al., 2019). On the other hand, chemisorption involved alteration in the chemical structure of adsorbate and adsorbent (Siddiqui et al., 2019). The physisorption is a rapid, multilayer, low-enthalpy process in comparison to slow, monolayer adsorption, and high-enthalpy process (Manceau, 1995).

3.7 Membrane Regeneration Studies

Adsorption/desorption of Cr (VI) by the PVA/SP-3 nanocomposite membrane was done in batch condition, and the result is shown in Fig. 3.28. The desorption studies were carried out in the presence of deionized water. The regeneratability of the PVA/SP-3 nanocomposite membrane was slightly decreased after the six-consecutive adsorptiondesorption cycles. Thus, PVA/SP-3 nanocomposite membrane can be repeatedly used for Cr (VI) adsorption without significant loss of its initial adsorption efficiency due to the stability of active sites available in the three-dimensional crosslinked polymeric network. The iron-silver magnetic binary oxide nanoparticle was effective for fluoride removal for up to six cycles during regeneration studies in the presence of sodium hydroxide (Azari et al., 2015).



Fig. 3.28: Repeatability of multifunctional PVA/SP-3 nanocomposite membranes for Cr (VI) removal.

3.8 Antimicrobial Properties

Antimicrobial properties of Ag/SP@PVA and Cu/SP@PVA nanocomposite membranes were determined. Fig. 3.29 refers to bacterial growth exposed to Ag/SP@PVA (a) and Cu/SP@PVA (b) nanocomposite membranes. While the growth of bacterial strains detached from Ag/SP@PVA (a) and Cu/SP@PVA (b) nanocomposite membranes after washing with PBS is given in Fig. 3.30. Bacterial growth was not observed in the presence of Ag/SP@PVA-1, Ag/SP@PVA-3, Cu/SP@PVA-1, and Cu/SP@PVA-3 nanocomposite membranes. Similarly, no bacterial growth was evident in the liquid PBS obtained after washing of the nanocomposite membranes.



Fig. 3.29a: Bacterial growth exposed to Ag/SP@PVA



Fig. 3.29b: Cu/SP@PVA (b) nanocomposite membranes.



Fig. 3.30: Growth of bacterial strains detached from Ag/SP@PVA (a) and Cu/SP@PVA (b) nanocomposite membranes after washing with PBS.

3.8.1 Scanning electron microscopy

Fig. 3.31 shows SEM of the surface of PVA/SP, Ag/SP@PVA, and Cu/SP@PVA nanocomposite membranes after incubation with cultures of *E. coli* for 20 h at 36°C (inoculum 10⁶ cells per mL). The surface of PVP/SP membranes showed bacterial colonization, while Ag/SP@PVA and Cu/SP@PVA nanocomposite membranes were almost clean except for a few cells and objects that are probably cell debris. The sepiolite fibers were also visible in the scanning electron micrograph of Cu/SP@PVA nanocomposite membrane.



Fig. 3.31: Scanning electron micrographs of PVA/SP (a), Ag/SP@PVA (b), and Cu/SP@ PVA (c) nanocomposite membranes cultured for 18 h at 37°C and pH 7 with 10⁶ cell/mL of *Escherichia coli* ATCC11775.

The summary of mechanisms responsible for bacterial growth inhibition is given in Fig. 3.32. Bacterial growth inhibition is induced due to contact of metal nanoparticles with the cell wall of bacteria either via electrostatic attraction (Li et al., 2015), van der Waals forces (Armentano et al., 2014), receptor-ligand, and hydrophobic interactions (Gao et al., 2014) and ultimately led to cell damage due to overproduction of reactive oxygen species (Fu et al., 2014). Secondly, the bactericidal and bacteriostatic effects of metal nanoparticles are caused by the inactivation of the metabolic enzymes, inhibition of DNA replication, interference with electron transport chain, membrane dysfunction as a result of metal binding on electronegative chemical groups, disruption of nutrient absorption and genotoxicity (Lin et al., 1998; Feng. et al., 2000; Salem et al., 2015; Shaikh et al., 2019). Thirdly, the release of metal ions or nanoparticles themselves disrupted the bacterial cell wall and altered the permeability of bacterial plasma membrane, and hence the bacterial cell death occurred (Singhal et al., 2012). Moreover, the internalization of metal nanoparticles via phagocytosis is responsible for their antibacterial activity (Akter et al., 2018). Table 3.5 shows the repeated inoculation and reuse of membranes with bacterial cultures up to five-time under favorable bacterial growth conditions.



Fig. 3.32: Mechanisms of action of metal nanoparticles for bacterial cell death (Shaikh et al., 2019).

Bacterial	Nanocomposite	Number of days				
strains	membranes	1	2	3	4	5
	Ag/SP@PVA-1	0	0	0	0	0
	Ag/SP@PVA-3	0	0	0	0	0
5. aureus	Cu/SP@PVA-1	0	0	0	0	0
	Cu/SP@PVA-3	0	0	0	0	0
	Control	3.62×10 ⁵				
	Ag/SP@PVA-1	0	0	0	0	0
	Ag/SP@PVA-3	0	0	0	0	0
B. cereus	Cu/SP@PVA-1	0	0	0	0	0
	Cu/SP@PVA-3	0	0	0	0	0
	Control	3.60×10 ⁷				
	Ag/SP@PVA-1	0	0	0	0	0
	Ag/SP@PVA-3	0	0	0	0	0
P. aeruginosa	Cu/SP@PVA-1	0	0	0	0	0
	Cu/SP@PVA-3	0	0	0	0	0
	Control	7.71×10 ⁶				
	Ag/SP@PVA-1	0	0	0	0	0
	Ag/SP@PVA-3	0	0	0	0	0
E. coli	Cu/SP@PVA-1	0	0	0	0	0
	Cu/SP@PVA-3	0	0	0	0	0
	Control	2.26×10 ⁷				

 Table 3.5:
 Repeated inoculation and reuse of membranes with bacterial cultures

3.9 **Project Results Dissemination/Outcomes**

3.9.1 Conference Presentations

Presented a paper titled "Metal nanoparticles; an alternative approach to fight bacterial infections" at the International Symposium on "Advances in Chemistry, Polymer Science and Biomedical Materials", pp. 71. September 24-26, 2019. (Venue: Pakistan Institute of Engineering and Applied Sciences, Islamabad) (Poster presentation).

3.9.2 Publications

- Nasir, A^Ψ., Masood, F^Ψ., Yasin, T., and Hameed, A. (2019). Progress in polymeric nanocomposite membranes for wastewater treatment: preparation, properties, and applications. (Ψ Both authors have made an equal contribution in this manuscript). Accepted in the Journal of Industrial and Engineering Chemistry. 79. 29-40. https://doi.org/10.1016/j. jiec.2019.06.052. Review article. (Impact factor; 4.97).
- Masood, F., Alam, A., Latif, N.A., Nasir, A., Yasin, T., Hameed, A., and Farooq, M. Tailoring and characterization of biofouling resistant Cu/SP@PVA nanocomposite membranes for effective removal of hexavalent chromium from wastewater. MEMSCI-2019-3520 (Manuscript submitted in Journal of Membrane Science).
- Masood, F., Affaqi, S.H., Latif, N.A., Yasin, T., Hameed, A., and Farooq, M. Effect of influence of Ag/SP and silane coupling agent on mechanical, biofouling resistant and chromium removal properties of PVA nanocomposite membranes. (Manuscript is under preparation).

3.9.3 Patent Filing

1. Masood, F., Yasin, T., and Hameed, A. Multifunctional nanocomposite membranes. Patent file is under preparation for submission to Pakistan Patent Office & US Patent Office).

4. SUMMARY AND CONCLUSIONS

Copper nanoparticles and silver nanoparticles were loaded into sepiolite by a simple, low-cost green chemical reduction method. TEM analysis indicated the formation of metal nanoparticles on the surface of sepiolite fibers. FTIR analysis of Cu/SP and Ag/ SP demonstrated a sharp decline in intensities of characteristic absorption bands of sepiolite due to ionic interactions of coordinating water molecules and zeolitic water molecules of sepiolite with CuO, Cu, AgO, and Ag nanoparticles. WAXD analysis of Cu/SP and Ag/SP showed a significant decrease in the intensities of characteristic reflections of pristine sepiolite due to the formation of Cu, Cu₂O, Ag/Ag₂O nanoparticles on the surface of sepiolite. It has been proved that the loading of metal nanoparticles into sepiolite fiber completely inhibited the growth of Escherichia coli ATCC11775 and Pseudomonas aeruginosa ATCC 27853 bacterial strains. The phase-inversion technique was used to prepare asymmetric PVA nanocomposite membranes. The variable concentration, i.e., 10 and 30 (% w/w) of sepiolite, Cu/SP, and Ag/SP was used to prepare the PVA/SP, Cu/SP@PVA, and Ag/SP@PVA nanocomposite membrane, respectively. The effect of concentration of TEOS on the degree of the crosslinking of the polymer matrix was also studied. A three-dimensional network structure with even distribution of pristine fibers and metal nanoparticles loaded sepiolite fibers were evident in the scanning electron micrographs of PVA/SP, Cu/SP@PVA, and Ag/SP@PVA nanocomposite membranes. FTIR spectra of PVA/SP nanocomposite membranes demonstrated a decrease in intensities of absorption bands in region at 3000-3600 cm⁻¹ (OH stretching vibrations), 1730 cm⁻¹ (-C=O- groups in -C=O-O-Cgroups), 1330 cm⁻¹ (stretch of -C-O- group in -C=O-O-H groups) with an increase in degree of crosslinking induced by crosslinking agent.

Additionally, the FTIR analysis of Cu/SP@PVA and Ag/SP@PVA nanocomposite membrane demonstrated the formation of coordination bonds between metal nanoparticle containing sepiolite and polymer matrix. A significant Cu nanoparticle leaching was detected from nanocomposite membranes using deionized water in comparison to Ag nanoparticles. The Cu/SP@PVA and Ag/SP@PVA nanocomposite membranes demonstrated potent antibacterial performance with complete removal of bacterial colonies detached from the membrane surface and in the liquid culture in contact with them. SEM images showed that Cu/SP@PVA and Ag/SP@PVA nanocomposite membranes were completely free of bacteria, as compared to the high colonization of PVA/SP nanocomposite membranes. The antimicrobial action was attributed to the release of metals diffusing from their supports. The nanocomposite membranes containing silver and copper sepiolite could be successfully reused after daily inoculations and subsequent washing up to 5 times with significant bacterial growth inhibition. The PVA/SP-3 nanocomposite membranes showed excellent

adsorption capacity for the removal of hexavalent chromium ions. The nanocomposite membranes demonstrated a good desorption profile using deionized water as well. In a nutshell, the designed polymer nanocomposite membrane is a good choice for the removal of chromium and bacterial strains, including *E. coli, S. aureus, P. aeruginosa,* and *B. cereus* from the wastewater. It would also be used for adsorption of other industrial effluents as well as in the controlled-release system.

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