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Electrospun nanofibers hybrid composites membranes for highly efficient antibacterial activity

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ABSTRACT

Safety of drinking-water is an urgent for human health. It is critical to promote the cheap technologies for water purification to guarantee the free-pathogens-drinking water. The present study has been investigated the antibacterial activity of polyacrylonitrile (PAN) nanofibers membranes which decorated by Ag, CuO or ZnO nanoparticles as bactericides. The hybrid nanofiber composites were fabricated by electrospinning technique and the obtained membranes were characterized using SEM, EDX and FTIR. Their antibacterial activity was evaluated against *E. coli* and *S. aureus*. The data was revealed that the functionalization was successfully obtained by the incorporation of nanoparticles as an additive into the polymer solution which associated many superior properties. Continuous PAN membrane fibers with average diameters from 170 to 250 nm without any beads of plain and its hybrid membrane composites were obtained. The antimicrobial activity was estimated using both disk diffusion tests and growth kinetic models. The antibacterial activity was improved as the concentrations of nanoparticles enhanced. This study provided the real solution for production and inactivation of bacteria which related to the impregnated the PAN nanofibers membrane with Ag, CuO or ZnO NPs. The results have significant implications for finding a safe and an inexpensive path to solve the problems of drinking water, especially in the developing countries.

1. Introduction

The availability of safe and clean water is an urgent request not only in rural and remote areas, but also at the flooding sites, mostly in developing and the least developed countries (He et al., 2018). The presence of bacteria in water (e.g., *E. coli)* is the main concern to the international economy due to their menace to human health (Liu et al., 2016; Li et al., 2017). Hence, it is an urgent request to provide a durable, reliable and strong disinfection route by developing an innovative, novel, effective, economical and environmentally friendly biocide with cutting edge characteristics for water disinfection (Jiang et al., 2016; Motshekga and Ray, 2017).

Separation by polymer membrane is the highest many-sided disinfection applications due to its high performance, environmentally friendly and ease of implementation, but cheap and highly efficient functional membrane for disinfection of large volumes of water are highly sought after. Recently, the advances in polymer nanocomposites have brought a hopeful solution for facing the current challenges which coming with the synthesis of high efficiency and multifunctional composites to solve the problems of the harmful disinfection byproducts (DBPs), controlling the spreading of diseases, high operating cost and time consuming that obtained from the traditional disinfection processes such as filtration, chlorination and ozonation (Unuabonah and Taubert, 2014; Mukherjee and De, 2017).

Polyacrylonitrile (PAN) is widely used as the main polymer for the synthesis of membranes for water filtration due to its highest mechanical strength and chemical stability (Wu et al., 2012). However, PAN membranes tend to be fouled rapidly by bacteria and proteins during the filtration process due to its high hydrophobicity (Zhao et al., 2012). The fouling may affect negatively on the permeability and the throughput of the membrane due to the aggregation of pollutants, especially bacteria in the pores of membrane or on the hydrophobic surface (Tang et al., 2016). Besides, potential secondary pollution, energy-intensive, shorter life span membrane, and lower water

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productivity, which is not only increases the operation cost but also shortens the life of the membrane (Matin et al., 2011). Two strategies for enhancing the properties of polymeric membranes; one is functionalization of the membrane via combination between the functions of metal or metal oxides and polymer for disinfection of bacteria (Tang et al., 2016). Another is the changing the properties of the surface of hydrophobic membrane into hydrophilic membrane (Chen et al., 2013).

Inorganic nanomaterials (metal and its oxides) have high activity due to its small particle size and high surface area (Horie and Iwahashi, 2014). ZnO and CuO appear to be an appropriate antibacterial disinfectant and their elements are very essential for human health (Raghupathi et al., 2011). The antibacterial activity of ZnO and CuO are highly significant due to that the Zn and Cu ions adhere to the bacterial cells, and penetrate the cellular membrane, which leading to the cellular disruption, DNA damage, and protein inhibition resulting in the killing of the bacterial cells (Ivask et al., 2010). Also, silver is an element with very specific bactericidal properties for inactivating a broad spectrum towards a wide range of microorganisms due to production of the reactive oxygen species (ROS) (Park et al., 2009). However, the practical application of these nanoparticles has still a challenge for the aggregation and dissolution (Faria et al., 2014). Hence, various polymeric materials such as poly vinyl chloride, poly acrylonitrile, poly vinyl acetate, alginate beads, chitosan, and cellulose are utilized as a matrix to improve the stability of CuO, ZnO and Ag NPs to enhance the disinfection ability of these hybrid composites (Lei et al., 2012; Jeon et al., 2008).

Research groups all over the world are investigating the synthesis of novel multifunctional nanomaterials (NMs) in order to make a progress in the disinfection systems and also remove/degrade the organic and inorganic pollutants from water. Nanofibers (NFs) have superior filtration characteristics. The versatility of being able to add functional molecules and chemical groups to the NFs, make it applicable for purification the water (Chauhan et al., 2017; Park and Kim, 2017). Anti-microbial nanofibers can be fabricated by incorporating nanobiocides into NFs. The formation of NFs with metal or metal oxides nanoparticles is well obtained due to its characteristics that involved with combining the functional properties of metal/oxide nanoparticles with the widely applicable properties of nanofibers (Chauhan et al., 2017; Zhang et al., 2011).

To date, few studies have been performed concerning the antibacterial activities of metal or metal oxide /polymer nanocomposites, although such studies are necessary and significant. Herein, it is in those perspectives as mentioned above, our objective is to prepare high disinfection materials, hybrid nanocomposite membranes, by incorporation Ag-NPs, ZnO NPs and CuO NPs on the surface of PAN nanofibers membranes via electrospinning with supported by various characterization techniques. These hybrid nanocomposites would be interesting for working as a disinfectant, including in membrane technology, which possesses interesting characteristics such as; environmental durability, excellent antibacterial activity and good mechanical properties. The synergistic effect of PAN nano fiber membrane and metal oxides or metal ions which led to a remarkable improvement in the antibacterial activity as compared to the pure PAN nanofiber membrane. The antibacterial activity of the prepared membranes was estimated versus different microorganisms that may pollute drinking water.

2. Materials and methods

2.1. Materials

Silver nitrate ($AgNO_3$; > 99.9%), zinc Nitrate hexa-hydrate ($ZnNO_3{\cdot}6H_2O$, 99.9%), copper sulfate 5-hydrate ($CuSO_4{\cdot}5H_2O$), sodium Hydroxide (NaOH, pellets), polyacrylonitrile (PAN, Mw 150,000 g/mol, Sigma-Aldrich), N,N′- dimethylformamide (DMF, 99.9%). All of these chemicals were of the highest purity available (Sigma-Aldrich, Germany).

2.2. Methods

2.2.1. Synthesis of zinc oxide nanoparticles (ZnO NPs)

ZnO NPs were prepared by one-pot chemical precipitation method. Briefly, a 0.45 M of $Zn(NO_3)_2{\cdot}6H_2O$ was dissolved in de-ionized water which heated at 55 °C. Then, 0.9 M of NaOH solution was added drop wise slowly to the above-heated solution under constant high-speed stirring. The beaker was sealed at this condition for 2 h to form zinc hydroxide as a precipitate. The white precipitate was filtered out and cleaned three times with deionized water and ethanol and dried in an oven at 200 °C 3 h. During this process, all zinc hydroxides were converted to zinc oxide to produce ZnO NPs, following the methodology adopted by Fazilati (2013).

2.2.2. Synthesis of cupric oxide nanoparticles (CuO NPs)

CuO NPs were prepared by chemical precipitation method. Briefly, a 0.4 M $CuSO_4{\cdot}5H_2O$ was dissolved in de-ionized water to heat at 85 °C and kept under constant high speed stirring till complete dissolving of the copper sulfate. After 15 min, 2 M NaOH solution as reducing agent was added, black precipitate was formed $Cu(OH)_2$. This precipitate was filtered out and washed with distilled water and ethanol several times, alternatively to remove possible remaining ions in the final product. After washing, the precipitate was kept in an oven at 200 °C for 3 h for decomposition. During this process all copper hydroxides were converted to CuO nanoparticles, following the methodology adopted by Suleiman et al. (2015).

2.2.3. Synthesis of PAN nanofiber hybrid composite membranes

2.2.3.1. Synthesis of pure PAN solution. PAN solution of 13 wt% were prepared using DMF as solvent that stirred at 80 °C for 6 h in well closed vial to avoid the evaporation of the solvent that may disturb the ratio. The obtained transparent homogenous solution was then cooled at room temperature.

2.2.3.2. Preparation of nanocomposite solutions. Firstly, ZnO or CuO NPs powder was firstly suspended in DMF with different percentage (1,2 and 3 w%) under continuous magnetic stirring. After complete dispersion of NPs, PAN was then added gradually at a concentration of 13 wt%. The solution was stirred at 80 °C for 6 h. The solution was then cooled at room temperature.

The same procedure was done for fabrication of Ag/ PAN nano fibers using the same homogeneous PAN solution containing 0.5 wt% of $AgNO_3$ in DMF.

2.2.3.3. Fabrication of nanofibers composites membranes. All mixtures were homogeneous, transparent, and free from all air bubbles or precipitates with suitable viscosity for spinning. Both the pure polymer solution and NPs suspended polymer solution were used for nanofibers composites fabrication using electrospinning, separately.

Each solution (pure PAN solution, PAN/ZnO, and PAN/CuO) was collected separately into a 10 ml syringe equipped with a 24-stainless steel blunted tip needle. PAN nanofibers were fabricated using the electrospinning technique in an air-conditioned laboratory. The process conditions were kept at an ambient temperature of 22 °C and relative humidity of < 65%. The syringe was fixed on an electric syringe pump set to maintain a constant feed rate of 1.5 ml/h. A high voltage power supply (Gamma high voltage, Inc., USA) was employed to apply positive charge to the needle, and a grounded metal plate covered with aluminum foil served as the collector. Electric potential and distance to collector was fixed at 20 kV and 13 cm, respectively.

On the other hands, for fabrication of Ag/PAN nanofibers, the same procedures were done except the exposure of the same PAN homogenous solution containing 0.5 wt% of $AgNO_3$ to UV irradiation for 3 and 6 h after electrospinning in order to complete silver ion reduction in the nanofibers to Ag NPs due to the $AgNO_3$ is photosensitive and decomposes in the presence of light. The UV irradiation using a tubular