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Investigation of characterization and biofouling properties of PES membrane containing selenium and copper nanoparticles

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ABSTRACT

Selenium and copper nanoparticles exhibit superior antioxidant activity, unique properties, and great potential applications that make them very attractive for developing new composite materials. In this study, polyethersulfone (PES) ultrafiltration membrane was modified by dispersing nano-sized selenium (nSe) and copper (nCu) particles uniformly in a PES solution (18% polymer weight) and casted by a phase inversion process. Membranes with four different weight ratios of nSe and nCu to PES of 0.002, 0.010, 0.030, and 0.050 were tested. Selenium nanoparticles were prepared by the reduction of aqueous sodium selenite solution with freshly prepared glucose solution. The method was capable of producing spherical selenium nanoparticles in a size range of about 150–175 nm, under ambient conditions. The synthesized nanoparticles can be separated easily from the aqueous solutions by a high-speed centrifuge and can be re-dispersed in an aqueous medium by an ultra-sonicator. The effects of temperature, time, and stirring rate on the size of the selenium nanoparticles were studied. In addition, nanoscale particles of metallic copper clusters were prepared by sonochemical reduction of copper(II) hydrazine carboxylate $Cu–(N_2H_3COO)_2 \cdot 2H_2O$ complex in an aqueous medium. Reduction process takes place under an argon atmosphere over a period of 2–3 h and the size of copper nanoparticles was about 90–105 nm. The synthesized selenium and copper nanoparticles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and particle size distribution techniques. Moreover, Se/PES and Cu/PES blend membranes were also characterized using contact angle goniometer, scanning electron microscopy (SEM), and permeation tests. Anti-fouling performance was examined using activated sludge as a biological suspension. The protein rejection study was also carried out using the bovine serum albumin (BSA) solution. The morphology and permeation properties of the blend membranes were found to be dependent on the amounts of nanoparticles. Compared to neat PES membrane, the 0.05 Cu/PES membrane exhibited highest protein rejection ratio (86.3%). However, the Se/PES membranes showed better antifouling performance (lower flux decline). The blending membranes with nanoparticles are considered to be suitable for the prevention of biofouling.

1. Introduction

The membrane processes have now become an attractive option for the treatment, separation, and reuse of municipal and industrial wastewaters. Membrane technologies are receiving special attention as alternatives to conventional water treatment and as a means of polishing treated wastewater effluent for reuse applications. However, widespread applications of membrane processes have been suffered due to membrane fouling. Therefore, efforts have focused on prevention of membrane fouling and increasing membrane flux as well as anti-fouling properties. Because membrane processes are considered key components of advanced water treatment, water reuse, purification, and desalination technologies, there is a continuous search for production of new materials and water treatment technologies [1].

Until now formation of biofilm on the surfaces and in the pores of membranes have long been identified as a main problem in membrane operation [2,3]. Biofouling can damage membrane surfaces, thus increasing membrane replacement costs and contributing

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to reduced membrane flux, resulting in higher operational costs [4]. Unlike physical or chemical fouling, biofouling is much more difficult to clean and often causes permanent permeability loss as well as irreversible damage of the membranes [5]. Nowadays polyethersulfone (PES) has become an important membrane separation material in order to have many good physico-chemical characteristics such as good heat-aging resistance and environmental strength as well as easy processing. However, the natural hydrophobicity of PES due to its structure provides to a low membrane flux and poor anti-fouling properties. Therefore, efforts have focused on to improve the properties of PES either by chemical or physical modifications [6]. For example, different methods were investigated to obtain a higher hydrophilicity of PES membranes. Rahimpour and Madaeni [7] prepared polyethersulfone ultrafiltration membranes with cellulose acetate phthalate and investigated the morphology, performance and anti-fouling properties of membranes. It was shown that the blending of cellulose acetate phthalate was one of the useful methods to prevent the membrane fouling. Rahimpour et al. [8] also investigated the fouling mitigation effect of immobilized TiO_2 UF membranes during the pasteurized and homogenized milk filtration. It was reported that a comparison between UV-irradiated TiO_2-entrapped and deposited membranes proved that coating TiO_2 on membrane surface was a superior technique for the modification of PES membranes to minimize membrane fouling. However, a hydrophilic, positively charged, quaternary ammonium derivative of a vinyl monomer, [2-(Acryloyloxy) ethyl] trimethyl ammonium chloride (AETMA) was used to modify a commercially available polyethersulfone (PES) microfiltration membrane by Malaisamy et al. [9]. AETMA-modified membranes were found to have a measurable antibacterial effect, whereas the AA-modified and unmodified membranes did not.

In recent years, research on the synthesis of nano-sized materials is of great interest due to their unique properties like magnetic, optical, electrical, mechanical, chemical, and biological characteristics as compared with raw materials [1,10]. The preparation of novel and specific organic–inorganic composite membranes has been a point of considerable interest over the last two decades. Moreover, by the way of blending nanoparticles, the modified membrane can combine basic properties of organic and inorganic materials and supply specific advantages with respect to thermal and chemical resistance, separation performances, fouling mitigation, and protection to the harsh wastewater environments [11,12].

Nowadays, metal nanoparticles such as silver, selenium, titanium dioxide, and zinc oxide have gained the attention of scientists because of their extensive application to new technologies in medicine, chemistry, biotechnology, electronics, textile, and engineering [13]. In this respect, selenium (Se) is one of the important nano materials [14]. Selenium is an indirect elemental semiconductor and exhibits good photoelectrical and nonlinear optical properties, high photoconductivity as well as catalytic activities towards organic hydration and oxidation reactions [15,16]. Moreover, Se has been successfully used by different researchers in the production of rectifiers, photovoltaic cells, xerography and so on [17–20]. Recent studies have shown selenium as an antimicrobial agent that inhibits the development of bacterial biofilm on a surface by acting as a catalyst for redox reactions involving reactive oxygen species [21–23].

In nature, selenium is present in igneous rocks and fossil fuels. It is a metalloid and exists as toxic forms like soluble selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}), and also as insoluble and nontoxic elemental selenium (Se^0) forms [24]. However, the synthesis and the chemical/physical properties of selenium nanostructures have not been widely investigated. Starting with suitable precursor, both oxidation and reduction techniques can be performed to prepare selenium nanoparticles [18]. A few reports have been published regarding the preparation of selenium nanoparticles. Among them vapor phase diffusion, physical vapor deposition, and wet chemical methods are significant and popular so far [25]. Bacterial reduction of selenite (SeO_3^{2-}) to Se^0 was also studied [24]. Some researchers have reported the synthesis of nanoselenium by oxidation of its precursors as well [26]. The main synthetic approach for preparing selenium nanoparticles is chemical reduction required reducing agent and stabilizer such as glycol, hydrazine, surfactant, high temperature etc [16,27].

During past years, synthesis of high-quality Cu nanoparticles as well as Se nanoparticles attracts much attention in both scientific and industrial field. Many attempts for synthesizing nano copper have been developed since 1990s, such as radiolytic reduction [28], electrochemical depositions [29], microemulsion techniques [30–32], reverse micelle systems [33], sonochemical method [34], hydrothermal method [35,36], chemical reduction [37,38], polyol processes [39–41], and vacuum vapor deposition [42,43].

Copper nanoparticles have been reported to be highly toxic against a wide variety of bacteria and fungus due to its high surface-to-volume ratio and generally kill cells by diverse mechanisms such as membrane disruption, blocking biochemical pathway, complex formation with proteins and DNA damage [44–46].

In this study, first, the synthesis of Se and Cu nanoparticles were performed under different conditions such as reaction temperature, reaction time, and stirring rate. The synthesized nanoparticles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and particle size distribution techniques. Second, the concept of introducing Se and Cu nanoparticles to PES polymer were investigated. The effect of polymer preparation conditions such as polymer concentration, solvent evaporation time, and nanoparticles concentration (up to 0.05 Se/PES or Cu/PES weight ratio in the casting solution) on the membrane permeation flux were studied. The membranes' morphology was characterized by scanning electron microscopy (SEM) and contact angle. Finally, investigation of fouling mitigation properties of Se or Cu entrapped PES membranes during the activated sludge filtration were also studied. Moreover, the protein rejection study was carried out using the bovine serum albumin (BSA) solution. The antibacterial properties of silver are well known, and silver nanoparticles (nAg) are now incorporated into a wide variety of consumer products for microbial control. However, to our knowledge, there is no any study reported in the literature to describe the effect of nanoselenium and nanocopper on the antifouling property of a polymeric membrane in activated sludge filtration for wastewater treatment.

2. Materials and methods

2.1. Materials

Sodium selenite (Na_2SeO_3), glucose, and *N*-Methyl-2-pyrrolidone (NMP) were purchased from Sigma-Aldrich used as received without further purification. Copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$) and hydrazine hydrate ($NH_2NH_2 \cdot H_2O$) were obtained from Merck. Polyethersulfone (PES ultrason E6020P with MW= 58,000 g/mol) was supplied by BASF Company. Distilled water used in all experiments was obtained with the two-stage Millipore Direct-Q 3UV purification system.

2.2. Synthesis of metallic nanoparticles

2.2.1. Selenium nanoparticles

Selenium nanoparticles were prepared by the reduction of aqueous sodium selenite (Na_2SeO_3) solution with freshly prepared