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Application of solution-blown 20–50 nm nanofibers in filtration of nanoparticles: The efficient van der Waals collectors

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ABSTRACT

In this work filtration efficiency of commercially available filter media with fiber/pore sizes of the scale of 10 μm is dramatically increased by not only adding electrospun nanofibers, as is usually done, but also a layer of ultrafine supersonically blown 20–50 nm nanofibers. Three different commercially available base filters were modified with (i) electrospun nanofibers alone, (ii) solution-blown 20–50 nm nanofibers alone, and (iii) the dual coating with electrospun nanofibers deposited first and the solution-blown 20–50 nm nanofibers deposited on top of them. Detailed observations of nanoparticle removal by these base and the above-mentioned modified filters revealed that the filters with dual electrospun nanofibers (deposited first) and the solution-blown 20–50 nm nanofibers deposited on top of them are the most effective in removing the below-200 nm Cu nanoparticles/clusters from aqueous suspensions. Experiments were conducted in two different time ranges: (a) for 8–15 s, and (b) for 8 min. It was found that the efficiency of the dual-coated filters containing 20–50 nm fibers was significantly higher than those of the others at the lowest nanoparticle concentrations of 0.2–0.5 ppm in suspension. The experiments conducted for longer time revealed that the smallest nanofibers were as efficient in particle retention as in the shorter-time experiments, and there was no visible breakage pattern of these nanofibers. The theory developed in the present work explains and describes how the smallest solution-blown nanofibers introduce a novel physical mechanism of nanoparticle interception (the attractive van der Waals forces) and become significantly more efficient collectors compared to the larger electrospun nanofibers. The theory predicts the domain of nanoparticle collection due to the van der Waals forces. The theory also elucidates the morphology of the nanoparticle clusters being accumulated at the smallest nanofiber surfaces, including the clusters growing at the windward side, or in some cases also on the leeward side of a nanofiber.

1. Introduction

Possibly the most important breakthrough that can be achieved using 20–50 nm fibers is in the area of filtration of micron- and submicron-sized particles. Over thousands of industries namely bio-medical, cosmetics, food processing, semiconductor, etc. use nanoparticles in their different processing units [1]. They require a high-level control over processes to eliminate the hazardous effects of nanoparticles, but still leach out nanoparticles from their units to the environment (air or water) [2]. In particular, these nanoparticles aerosolize in air. Often nanoparticles in the range 10–50 nm form clusters and make submicron-sized particles of ~500 nm, which are very hard to break [1,2] owing to strong van der Waals interactions between them. Combustion products often aggregate to form such agglomerates. Sub-micron-sized soot particles are considered very hazardous to breathe as they are detrimental for proper functioning of alveoli in lungs above a certain limit [3]. Not only airborne, but also waterborne or surface-borne nanoparticles are potential hazards. Manufactured nanoparticles have their detrimental effects on aquatic organisms [4,5]. Different nanoparticles like silver or Ti which are often used as antibacterial or antifouling agents remain in the water stream [6], and above a certain limit of 10 μg/l these nanoparticles are potential threats to swallow. The ceramic membranes employed for water filtration leach out these nanoparticles. Then, the nanoparticles enter human body via drinking water. All these nanoparticles, which are either washed from industrial units or generated by other sub-processes, end up accumulating in living organisms. Even the most efficient HEPA filters have the maximum

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efficiency for particles larger than 0.3 μm [1]. Surprisingly, there is almost no information or regulations on specific nanoparticle sizes in filtration of drinking water, and focus has been mostly on micron-sized particles, whereas in reality submicron-sized particles and pathogens (microbes, bacteria, viruses, etc.) are frequent among harmful waterborne particles.

For the last two decades electrospinning has gained immense popularity in producing filter media for capturing micron and submicron particles [7–9]. Electrospun membranes have been used mostly as pre-filters, especially after asbestos fibers were proven to be detrimental and were replaced by the polymeric fiber membranes [10]. However, the strength issues related to those fibers are one of the main concerns when liquid is pressurized for separation [1]. For different grades of filtration, for example, for ultra-filtration or micro-filtration, the usage of electrospun membranes has thus been limited to a sandwiched layer [11]. Donaldson Inc. is one of the forerunners in using nanofibrous media in filtration, and currently there are several other industries which use them for filtering application [1]. Nanofibrous media have multiple applications in transportation air filtration [12], dust collection [13], liquid filtration, smoke filtration, and coalescence filters [14]. Research has been also conducted on commercial HEPA filters with electrospun layers. It was shown that these are better performing filters than the previously used ones [15] mostly due to the modified porosity with a larger surface area. However, nanofibers in a filter also increase pressure drop, especially in coalescence filters [14]. Even in air filtration nanofibers rapidly result in a cake-like structure formation and block the flux. With air particulate filtering, flow reversal (pulsing) to brush off the collected particles and to regain filter efficiency is quite natural, albeit it is uneasy in regards to filtration of waterborne particles.

Though different filter media remove particles from the stream differently, they all involve such common mechanisms as the inertial impaction, direct interception or Brownian motion [7]. The smallest particles, in the range ~10 nm, are commonly caught due to Brownian motion (diffusion) [16]. Particles in the range of microns are commonly captured by sieving or inertial impacts. The particles in the mid-range are regularly intercepted by big fibers, if not by impact then just by brushing along the fiber surface. The most penetrating particle size for air filtration has been found as 0.3 μm. However, as mentioned earlier, water filtration still lacks such precise data on the most penetrating particle size. Also, for particle separation from liquid, the scenario is far worse, since particle diffusion is much slower in liquid and inertial impacts are not as helpful as normal sieving mechanism [17]. There are several other mechanisms important in filters, like electrostatic double-layer interaction, etc. Note also that one of the frequently used options to intercept the smallest nanoparticles is an increase in the filter media thickness, which, however, also results in higher pressure drop to sustain a given flow rate, which is undesirable.

The van der Waals interactions between nanofibers and nanoparticles represent another mechanism which is responsible for particle agglomeration in the filter media [18]. Nanofibrous prefilter media can be a potential area where the van der Waals interactions can become effective due to a tremendous surface area to volume ratio. Though the van der Waals interactions are weaker in comparison to those responsible for the common mechanisms of direct impact or interception, this mechanism can be useful when the particle-to-fiber diameter ratio is close to 1, and indeed in such cases the smallest fibers (~50 nm) can act as potential "magnets" in the fibrous media, as demonstrated in Sections 3–5 below. A number of numerical and analytical studies dealt with the effect of the van der Waals forces on the interception of particles of the sizes ~100 nm [19–24]. It was also shown theoretically that as the fiber size would diminish to the 20–50 nm range, the capture efficiency of nanoparticles of the size 10–100 nm would increase by an order of magnitude [20]. It should be emphasized that electrospinning can produce fibers in the range of 100–300 nm, however, fibers in the range of 20–50 nm cannot be normally produced by electrospinning [25]. In the previous work of this group [26] it was shown that supersonic solution blowing is capable of routinely producing nanofibers in the 20–50 nm range. To the best of our knowledge, no other methods are available for modifying filter media with such nanofibers. Accordingly, it is expected that a single-layer mat of 20–50 nm nanofibers deposited by supersonic solution blowing on a commercially available filter can be sufficient to raise the efficiency from a moderate one without increasing the pressure drop. This can scavenge the midsize (~0.3 μm) or smaller nanoparticles and make clusters of them, still without fouling the filter. The present work aims at this goal. Section 2 describes the experimental methods employed. The experimental results are presented and discussed in Section 3. The theoretical aspects and comparisons with the experimental data are presented in Section 4, and conclusions are drawn in Section 5.

2. Experiments

2.1. Materials

The experiments were conducted using three different grades of commercial filters: (1) glass filter-GC90 of 90 mm diameter, and mean pore size 2.7 μm and thickness 1 mm, and (2) cellulose filters of mean pore size 17 μm, thickness 0.6 mm (referred to as *cellulose a* later), and (3) of mean pore size 2.5 μm, thickness 0.61 mm (referred to as *cellulose b* later). Polyacrylonitrile (PAN) (molecular weight 130 kDa) solution in N,N-dimethylformamide (DMF) was used to form polymer nanofibers by electrospinning and deposit them on top of the above-mentioned filters. Both PAN and DMF were obtained from Sigma-Aldrich. Nylon 6 (molecular weight of repeat unit 104.8 Da) was used as a polymer to form nanofibers by means of the electrically-assisted supersonic blowing [26]. These nanofibers were deposited on top of the filters as well, either directly, or on top of the electrospun PAN nanofibers. Nylon 6 was also used for electrospinning in additional experiments to produce filters with both solution-blown and electrospun nylon 6 nanofibers deposited on the base filter medium. Nylon 6, along with its solvent formic acid, was obtained from Sigma-Aldrich. Polypropylene filter holder (47 mm), obtained from Cole – Parmer was used in filtration experiments. Aqueous suspensions of copper nanoparticles, obtained from Skyspring Nanomaterials (~40–60 nm, as per manufacturer), at different concentrations were used as the suspensions to be filtered. Also, aqueous suspensions of polystyrene 100 nm nanoparticles, from Microspheres – Nanospheres were used.

2.2. Electrospinning

Electrospinning of 12 wt% PAN, dissolved in DMF and mixed for 24 h using a magnetic stirrer, was conducted using a syringe pump (obtained from New Era Pump System) pushing the polymer solution through an 18 gauge needle at a flow rate of 0.5 ml/h. The distance between the collector and the needle was kept at 12 cm and the electric field strength was sustained at 1.2 kV/cm. The collector was mainly an aluminum foil. The above-mentioned filters, cut in 47 mm circles, were placed carefully on the foil so that the electrospun fibers can be collected on the filters as well (cf. Fig. 1). Electrospinning was conducted for 45 s on each of the filter samples, which resulted in a very thin layer of nanofibers on the filters. After electrospinning was finished, the samples were carefully removed without damaging the fiber layers.

Nylon 6 was also eletrospun to obtain results for Table 1.