ELEKTROSPINNING TEKNİĞİ VE UV İŞIMASININ EŞZAMANLI OLARAK UYGULANMASI İLE NANOFLBER MEMBRANLARIN HAZIRLANMASI VE KIYMETLİ METALLERİN ADSORPSİYONUNDA UYGULANMASI

ÖZET

Nanofiber membranlar, her türlü ihtiyaca uygun işlevsellikleri, eşsiz mekanik ve yüzey özelliklerinden dolayı günümüzde adsorpsiyon, filtrasyon, doku mühendisliği, sensörler, polimerik piller, kompozit destekleyicisi olarak birçok uygulama alanında kullanılmaktadır. Nanofiber üretiliminde en fazla tercih edilen "Elektrospinning" tekniği, fiber çaplarının nano boyutta olması en etkili, basit ve çok yonlu bir tekniktir. Bu hızla gelişen teknik ile elde edilen fiberlerin özelliklerinin iyileştirilmesi için bir çok modifikasyon yapılabilmiştir.

Polivinil alkol (PVA), organik ve inorganik maddelerle kolaylıkla reaksiyona giren, biyo-uyumlu ve toksik olmayan, kimyasal ve termal kararlılığı iyi olan bir polimer olarak bilinmektedir. PVA'nın yapısında bulunan fonksiyonel hidroksil (–OH) grupları kolaylıkla modifiye edilebilir, böylece polimerin çapraz bağlı yaparak daha kararlı bir yapı oluşturması sağlanmaktadır. Bu özellikleri sayesinde birçok alanda kullanılabilir. nanofiber membranlarının sentezlenmesi için oldukça uygun bir polimer olarak görülmektedir. Adsorpsiyon amaçlı sentezlenen nanofiberlerin, çeşitli fonksiyonel gruplarla (tiyol (–SH), tiyoter (–S–) ve amino (–NH₂) gibi) modifiye edilerek adsorpsiyon özellikleri geliştirilmekte ve kapasiteleri arttırmaktadırlar. Böylece sentezlenmiş nanofiberler her türlü endüstriyel atık sulardan organik ve inorganik kirleticileri uzaklaştırmak ve/veya geri kazanmada rahatlıkla kullanılmaktadırlar.


Karakterizasyon işlemlerini tamamlanan nanofiber membranların adsorpsiyon kabiliyetleri incelenmiştir. Sentezlenen membranlar arasında Pt (IV) ve Pd (II) iyonları için sırasıyla % 72 ve
PREPARATION OF NANOFIBER MEMBRANES BY THE IMPLEMENTATION OF ELECTROSPINNING TECHNIQUE AND UV RADIATION SIMULTANEOUSLY AND APPLICATION ON ADSORPTION OF PRECIOUS METALS

SUMMARY

Nowadays nanofiber membranes, due to the functionality to suit all needs, unique characteristics of the mechanical and surface properties, have found applications in many different areas. When the diameters of fiber are shrunken from micrometers (e.g. 10–100 μm) to submicrons or nanometers (e.g. 10×10−5–100×10−9 μm), there appear several amazing characteristics such as very large surface area to volume ratio (this ratio for a nanofiber can be as large as 10³ times of that of a microfiber), flexibility in surface functionalities, and superior mechanical performance (e.g. stiffness and tensile strength) compared with any other known form of the material. A number of processing techniques such as drawing, template synthesis, phase separation, self-assembly, electrospinning, etc. have been used to prepare polymer nanofibers in recent years. The drawing is a process similar to dry spinning in fiber industry, which can make one-by-one very long single nanofibers. However, only a viscoelastic material that can undergo strong deformations while being cohesive enough to support the stresses developed during pulling can be made into nanofibers through drawing. The template synthesis, as the name suggests, uses a nanoporous membrane as a template to make nanofibers of solid (a fibril) or hollow (a tubule) shape. The most important feature of this method may lie in that nanometer tubules and fibrils of various raw materials such as electronically conducting polymers, metals, semiconductors, and carbons can be fabricated. On the other hand, the method cannot make one-by-one continuous nanofibers. The phase separation consists of dissolution, gelation, extraction using a different solvent, freezing, and drying resulting in a nanoscale porous foam. The process takes relatively long period of time to transfer the solid polymer into the nano-porous foam. The self-assembly is a process in which individual, pre-existing components organize themselves into desired patterns and functions. However, similarly to the phase separation the self-assembly is time-consuming in processing continuous polymer nanofibers. Electrospinning is a simple, convenient, effective and widely utilized technique for generating nanofiber membrane materials, and has attracted a great deal of attention in recent years. Many modifications have been made to improve the properties of nanofibers produced by this rapidly developing technique. Thus, the electrospinning process seems to be the only method which can be further developed for mass production of one-by-one continuous nanofibers from various polymers. As the usefulness of other processes is also limited by combinations of restricted material ranges, possible fiber assembly, cost, and production rate, electrospinning has an advantage with its comparative low cost and relatively high production rate.

The electrospinning technique has been developed for the synthesis of nanofibers since 1934. This process utilizes a high voltage source to inject charge of a certain polarity into a polymer solution or melt, which is then accelerated toward a collector of opposite polarity. As the
electrostatic attraction between the oppositely charged liquid and collector and the electrostatic repulsions between like charges in the liquid become stronger the leading edge of the solution changes from a rounded meniscus to a cone (the Taylor cone). A fiber jet is eventually ejected from the Taylor cone as the electric field strength exceeds the surface tension of the liquid. The fiber jet travels through the ATUosphere allowing the solvent to evaporate, thus leading to the deposition of solid polymer fibers on the collector. Fibers produced using this process typically have diameters on the order of a few micrometers down to the tens of nanometers.

The electrospun nanofibers exhibit special characteristics, such as high specific surface area per unit mass, high porosity, high gas permeability and small interfibrous pore size. Due to these important properties they have a wide range of applications, such as in drug-delivery systems, scaffolds in tissue engineering, enzyme and catalyst support, clothing protection, wound dressings, sensors and electronic and optical devices, filtration media and water treatment.

Based on the above properties, the nanofiber membranes have been speculated to have high adsorption capacity. For the removal/adsorption of specific materials from waste/aqueous solutions, generating polymer nanofiber membrane materials having rationally designed high porosity, high surface area, high adsorption capacity and regeneration still remains a challenge. To increase the adsorption of metal ions on nanofiber materials, the following methods have attracted the most attention: (1) surface modification with functional groups and (2) increasing the surface area of nanofibers. Mesoporous nanofibers modified by functional groups have attracted much attention because of their properties such as: (1) high surface-to-volume ratio, (2) uniform pore size distribution, (3) convenient recycling, and (4) high equilibrium adsorption capacities for heavy metal ions.

More than 100 polymers, both synthetic and natural, have been successfully electro-spun into nanofibers, mostly from polymer solutions since any polymers may be electro-spun into nanofibers, provided that the polymer molecular weight is sufficiently high and the solvent can be evaporated in time during the jet transit period over a distance between the spinneret and the collector. Standard polymers successfully electro-spun into nanofibers include: polyacrylonitrile (PAN), poly(ethylene oxide) (PEO), poly(ethylene terephthalate) (PET), polystyrene (PS), poly(vinyl chloride) (PVC), Nylon-6, poly(vinyl alcohol) (PVA), poly(e-caprolactone) (PCL), Kevlar (poly(p-phenylene terephthalamide), or PPTA), poly(vinylidene fluoride) (PVDF), polybenzimidazole (PBI), polyurethanes (PUS), polycarbonates, polysulphones, poly(vinyl phenol) (PVP), and many others.

Poly (vinyl alcohol) (PVA) is a highly biocompatible and non-toxic, semi-crystalline hydrophilic polymer with good chemical and thermal stability. It is known to easily interact with other organic and inorganic materials. The functional hydroxyl group (−OH) in PVA structure can be easily modified, by crosslinking of the polymer which provides a more stable structure. When the electrospun PVA nanofiber membrane was immersed in water, it would dissolve because PVA is a water soluble polymer. Therefore, it is necessary to crosslink the PVA polymer and stabilize the electrospun nanofiber membranes in wet condition. All multifunctional compounds capable of reacting with the hydroxyl group may be used as a cross linker of PVA such as dialdehydes, dicarboxylic acids, dianhydrides. The adsorption capacity of PVA nanofibers used for adsorption is increased by modification with functional groups such as thiol (−SH), thioether (−S−), and amino (−NH₂) groups which contain S and N donor atoms. Hence,
nanofibers are quite widely used to remove and/or recover the organic and inorganic pollutants from all kinds of industrial wastewaters.

In this study, pure PVA and UV-curable poly(vinyl alcohol)/maleic anhydride/acryloyl thioamide monomer (PVA/MA/ATU) nanofiber membranes were synthesized by electrospinning technique. For this electrospinning method was combined with UV radiation technique. *In situ* UV radiation was applied during the electrospinning in order to provide polymerization of the jet during its flight and promote crosslinking of ATU and MA with PVA. The cross-linking was examined by Fourier-transform infrared spectroscopy (FTIR). The morphology and thermal behavior of electrospun nanofiber were characterized by scanning electron microscope (SEM) and thermogravimetric analysis (TGA), respectively. The surface area of nanofiber membranes was measured by Brunauer–Emmett–Teller (BET) analysis. Furthermore, water durability test was examined. Water durability test demonstrated that *in situ* photo-cured PVA/MA/ATU nanofiber membrane had the least average mass loss. The surface areas of PVA/MA/ATU nanofiber membranes were 160-280 m²/g. The surface areas and diameters of PVA/MA/ATU nanofibers decreased as the PVA content increased. The results showed that the water-insoluble nanofiber membranes with better chemical and thermal resistance were obtained.

The adsorption capabilities of nanofiber membranes completed characterization operations were examined. The highest adsorption yield for Pt (IV) and Pd (II) ions was obtained by 9% PVA/MA/3ATU nanofiber membranes. These membranes were used for the adsorption-desorption of Pt (IV) and Pd (II) ions from dye assay leaching solution. Adsorption isotherms, kinetic and thermodynamic calculations for the adsorption process were also studied. After adsorption process, the structure and surface morphology of PVA/MA/ATU nanofiber membranes were analyzed by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy-energy dispersion spectrometry (SEM-EDS). The adsorption equilibrium data fit better using the Langmuir model than the Freundlich model. Maximum adsorption capacities, Qmax, at 45°C were found to be 69.93 and 112.36 mg/g for Pt (IV) and Pd (II), respectively. The activation energies (Ea) of Pt (IV) and Pd (II) were 27.90 kJ/mol and 20.29 kJ/mol, respectively. Thermodynamic study revealed that the adsorption process is spontaneous in nature. The best desorption reagent was a 1.0 M HCl-1.0 M TU solution for both Pd (II) and Pt (IV). Desorption results showed that the adsorption capacity can remain up to 90% after 5 times of usage.