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Electrospun nanofibre membranes for textile wastewater treatment

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Abstract. Among the many uses of electrospun membranes, wastewater treatment is one of the most important, because of their special qualities (large surface area, great porosity, outstanding pore interconnectivity). In the textile industry, wastewater treatment is of utmost importance, especially for recycling purposes. This paper reviews the ways of obtaining these electrospun membranes and the possibilities for their use in the treatment of textile waste water, with a special emphasis on removing the colour of these waters.

1. Introduction

Synthetic dyes are, for more than 150 years, a common presence in people's lives. Dyes are used in a wide range of industries: textiles, leather, food, cosmetics. The amount of dyes used globally is huge: over 100,000 tons of dyes (more than 90,000 only in China) [1] with a great diversity of chemical structure are estimated to be produced annually. More than 10,000 tons of these dyes are found in the wastewater as a result of imperfect fixing on the substrate [2].

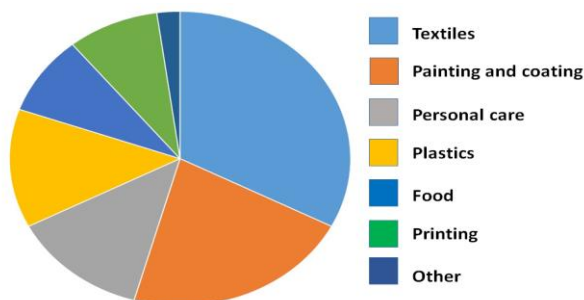


Figure 1. Global dyestuffs consumption in industries [3].

The textile industry uses enormous amounts of dyes, characterized by various chemical structures. These colorants are intended primarily for dyeing cellulose fibres (direct dyes, reactive, vat, sulphur), protein and polyamide fibres (acids, metal complex), polyester fibres (disperse dyes) or acrylic fibres (basic dyes). As a result of incomplete exhaustion, significant amounts of these dyes are found in textile wastewater. Their presence is undesirable for aesthetic reasons, but also due to the fact that the colour reduces the penetration of solar radiation into water, affecting photosynthetic processes. Textile wastewater does not usually contain pollutants that are difficult to remove in the primary or biological

treatment stages. The same can not be said for the synthetic dyes, mostly refractory to biological degradation, which implies the use of special colour removing methods [4-10]. The methods for treating coloured wastewater fall into the following main categories: adsorption, coagulation, oxidative processes or membrane separation. Membrane separation is one of the most effective methods of discolouration of dye containing waters, and the effectiveness of the process is often enough to ensure even recirculation of the treated waters.

Electrospun nanofibre products are among the most used materials for such membranes - by nanofibres meaning fibres having diameters less than 1 μm [11-14]. Electrospinning is a relatively new, but very efficient process of producing nano-diameter filaments by forcing a solution or polymer melt through a nozzle, as a high voltage is applied between the polymer reservoir and the collector (typically between 10-50 V). The extrusion force is generated by the interaction between the charged polymer fluid and an external applied electric field. When a polymer solution is used, the solvent evaporates before reaching the collector and micro or nano-sized fibres are collected. The main parameters that influence the electrospinning process are the characteristics of the solution or the polymer melt (concentration, conductivity), the parameters of the type-to-collector process (applied voltage, feed flow rate, tip-to-collector distance) and the ambient conditions (humidity and temperature).

2. Electrospinning techniques

Electrospinning is considered to be the most proficient method for nanofibres production [15-17]. The electrospinning process offers high versatility of the nanofibre formation, with accurate control over the porosity, pore size, surface properties, and mechanical and thermal stability.

The basic electrospinning system consists of following parts: the polymer reservoir, a spinneret, an injection pump, the high-voltage power supply that creates a strong electrostatic field that charges the polymer and a collector [18-21]. These basic parts are shown in Figure 2.

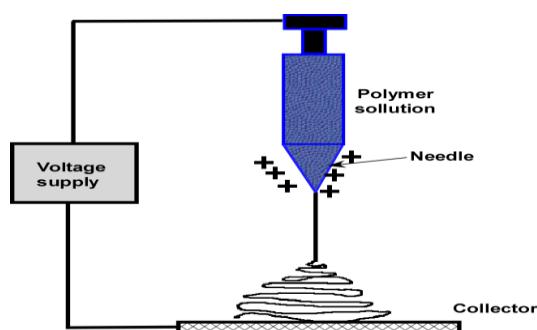


Figure 2. Typical electrospinning setup.

This basic scheme knows many variants in all of its components, but especially in the polymer extrusion part and in the electrospun nanofibres collection.

In the first case, it is about multiple needle electrospinning, coaxial or needleless electrospinning. Various collector geometries have been used to obtain defect-free fibres with precise dimensions and orientations such as rotating drum or wire drum, parallel collectors, knife-edge collectors, discs, electrode arrays, ring collectors [22-25].

3. Electrospun membranes in wastewater treatment

The nanofibre membranes made by electrospun have extraordinary properties such as great specific surface area [26-29], high porosity with fine pores, interconnected pore structure [30-33] and sufficient mechanical strength, and they are easy to produce and functionalize. These properties make them attractive for resolving environmental problems such as water and wastewater-related issues because of their high efficiency [34-36]. The membrane separation processes that are used for

wastewater treatment are, in order of increasing separation capacity, microfiltration, ultrafiltration, and nanofiltration and reverse osmosis, [37-39]. Due to their special features, electrospun membranes proved to be efficient adsorbent of heavy metal ions from wastewater [40, 41]. Electrospun PEO/Chitosan and chitosan/poly(vinyl alcohol) nanofibre membrane were used for the removal of heavy metal ions (copper, lead, cadmium and nickel) from water, showing good removal capacity, especially for nickel, with up to five cycles reusability of the membrane [37, 42].

To remove heavy metal ions poly(vinylidene fluoride) and ethylenediaminetetraacetic acid electrospun nonwoven mats have been tested, which proved high efficiency in removing Fe, Cr, and Ni, acting through a chelation mechanism. Up to 60 % of heavy metal ions can be removed after 30 cycles of chelating filtration [43]. Electrospun polyindole nanofibres attested to be efficient in removing Cu(II) from wastewater, and the process was feasible and spontaneous, as the adsorption capacity remained up to 75 % after 10 cycles [4]. Membranes from electrospun polyvinyl alcohol/chitosan/zinc oxide/aminopropyltriethoxysilane were successfully used to remove cadmium and nickel ions from wastewater [44-47]. Electrospun membranes made from polyvinyl alcohol and karaya, a natural gum, also effectively removed metal nanoparticles (Ag, Au, Pt, Fe₃O₄ and CuO) from aqueous solution [48-53]. Electrospun poly(vinyl alcohol)/tetraethyl orthosilicate/aminopropyltriethoxysilane nanofibre membranes were used to remove uranium from aqueous solution, showing good regeneration capacity and insignificant decrease in their performance after five treatment cycles [54].

Electrospun nanofibrous polyamide 6 membranes have been used in Membrane Bioreactor after heat-treating. The heat treatment prevented the fast flux decay, improving the integrity and mechanical strength of membranes [55]. Electrospun membranes from polymers like polystyrene, poly(vinylidene fluoride), or poly(tetrafluoroethylene) have been used for oil/water separation, proving high efficiency [56-58]. Even higher superhydrophobicity and superoleophilicity of the electrospun membranes was obtained when a silver coating was applied, which lead to a capacity of up to 30 cycles of treating oily wastewater with good stability [59]. When treating with UV, the polyurethane and poly(diacetylene) electrospun membranes developed higher mechanical resistance (over 1000 stretching cycles) [60].

Membranes made of electrospun nanofibres of alkali lignin and poly(vinyl alcohol) co-polymer showed good adsorption capacity for pharmaceutical contaminant (fluoxetine) after a contact time of only 1 h [61]. Nylon 6 electrospun nanofibres membranes effectively removed oestrogens from water, and their efficiency remained up to 80% after seven times usage [62].

4. Electrospun membranes in textile water and wastewater treatment

Membrane separation is a usually applied method for textile wastewater treatment, especially for colour removing. In this area electrospun membranes find extensive applicability.

Electrospun membranes made of poly(vinyl alcohol) and polyurethane respectively were used to retain reactive dyes from wastewater, and it was found that the maximum sorption capacity was 88.31 mg/g. This performance was attained when poly(vinyl alcohol) was cross-linked with 1,2,3,4 butanetetracarboxylic acid [63]. Electrospun fibroin/polyacrylonitrile nanofibrous membranes containing polyaniline/TiO₂ nanoparticles proved to be efficient in removing reactive dyes from wastewater (up to ~92% dye removal at pH = 3) [64]. Sericin/poly (vinyl alcohol) electrospun nanofibres have been used as well to remove colour from textile wastewater [65]. Polyacrylonitrile/poly(amidoamine) blend electrospun nanofibre mats proved to be efficient adsorbent for reactive dye removal [66]. The colour of reactive dyeing wastewaters can also be removed using a phthalocyanine functionalized electrospun cellulose nanofibre mats under basic conditions, when more than 90 % of dye was eliminated in less than 12 min [67].

Membranes from diethylenetriamine/polyacrylonitrile electrospun composite nanofibres were used to remove colour from direct dyeing wastewater. The quantity of dye adsorbed onto the membranes was influenced by the pH of the solution, the initial dye concentration and the contact time [68]. Electrospun fibres of methacrylic acid and methyl methacrylate copolymers were used for the removal of direct dyes, resulting in maximum adsorption capacity of 135.37 mg/g [69]. Efficient direct dye

removal from textile wastewater was achieved using chitosan/poly(vinyl alcohol) high-performance electrospun nanofibrous membranes [70, 71]. The colour removal capacity increased when the membrane incorporated SiO₂ nanoparticles [72]. Another chitosan based nanofibre composite nano-filtration membrane was prepared by a combination of grafting, electrospinning and surface coating. The membrane, which showed very good tensile mechanical properties and high porosity, could be used to effectively remove direct and reactive dyes from wastewater [73]. Poly(ethylenimine) electrospun nanofibres showed effective capacity of removing direct dyes from aqueous solution, reaching an adsorption capacity of 633.3 mg/l [74]. Even pigments found in textile wastewater could be removed using a electrospun Nylon 6 nanofibre membrane, which showed lower flux compared to a commercial membrane, but gave better removal of suspended solids [75-80].

5. Conclusions

Electrospun nanofibres membranes are becoming more and more widely used in the field of wastewater treatment. One area of particular interest is the discoloration of textile wastewater, where this type of membrane records remarkable results. High colour removal efficiency has been achieved with reactive dyes, widespread dyes with significant discoloration difficulties, and direct dyes. It is to expect that in the future the features of electrospun membranes to be further enhanced, by applying additional methods like using dopants or in situ polymerization.

6. References

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