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Electrospun polystyrene-(emeraldine base) mats as high-performance materials for dye removal from aqueous media

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A B S T R A C T

A more widespread use of conducting polymer nanostructures in environmental remediation is limited by their tendency to form agglomerates. In this study, we report the development of electrospun polystyrene/polyaniline composite membranes that can be used as efficient agents for the removal of dye molecules from aqueous solutions. These nonwoven polystyrene-polyaniline (NW PS-PANI) mats are formed after the incorporation of the conducting polymer into the surface of nonwoven polystyrene (NW PS) mats produced *via* the electrospinning method. The composite mats were characterized by contact angle measurements, SEM, FTIR and UV–vis spectroscopy. By performing experiments in batch mode, we examined the capacity of these mats for removing Congo red (CR) molecules, a prototypical azo dye, as a function of pH, interaction time and dye initial concentration. These membranes are hydrophilic and have a large CR removal efficiency. The zero point charge pH of the NW PS-PANI membranes was determined as 6.4, and we have found that their adsorption capacity reaches a maximum of 380.0 mg/g at pH 6.0. An easy recovery of the contaminant is possible by using these mats, which can be reutilized in at least 13 consecutive adsorption/desorption cycles, without significant losses in their adsorption capacity. In addition, they can be adapted for usage in compact filtration systems for an even faster removal of the dissolved dye molecules.

1. Introduction

Water pollution is a major global problem, whose severity has dramatically increased with the continuous population growth and the accelerated industrial development observed in the last decades. Worldwide, water contamination is responsible for 1.6 million of human deaths every year [1], which can be associated with the presence of pollutants of a varied nature, such as organic matter [2], pathogenic microorganisms [3,4], and chemical residues (mostly drugs, dyes and heavy metals) [5–8]. Non-biodegradable chemical pollutants can remain reactive in the environment for years, while organic dyes have extensive presence in the wastewater of the textile, paper, plastic, leather, food, pharmacy, and cosmetic industries [9–12]. When dissolved in aqueous media even in concentrations as low as 1 ppm, azo compounds such as Congo red can endanger the ecosystem through an ecological imbalance caused by the decrease in sunlight penetration on the water body, which reduces photosynthesis and oxygenation rates [13,14]. Moreover, azo dye molecules present in drinking water can accumulate in living organisms and eventually lead to the long-term development of cancer in humans [7,15]. In fact, several consolidated technologies for wastewater remediation exist today. The interested reader can find appropriated references, for instance, in the work of Gupta and collaborators concerning the use of TiO_2 particles, carbon nanotubes and waste materials for the treatment of dye and heavy metal contamination of water resources [8,10–12,16–18]. However, it seems likely that some of the current separation methods [18] will become obsolete in the coming years due to the growing demand for high quality water that should be obtained at lower costs and by use of less energy consuming methods [19].

Nanotechnology holds the promise of providing for new materials that could be used to address those issues by allowing both the improvement of the current purification methods and the creation

Abbreviations: NW, nonwoven; PS, polystyrene; PANI, polyaniline; CR, Congo red; ES, electrospinning; ICPs, intrinsically conducting polymers.

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of innovative wastewater remediation processes. Due to their intrinsic sizes, nanostructures possess high surface area and exhibit properties that are novel when compared to those of equivalent materials in their bulk form, such as peculiar optical and magnetic characteristics [20,21]. In terms of water remediation, two approaches employing nanomaterials deserve special mention. One is based on the use of magnetic nanoparticles modified with ligand agents on their surfaces, a technology that has several inherent advantages for its practical implementation, such as low cost and an easy retrieval of the nanoparticles by the direct application of an external magnetic field [22].

An alternative approach involves the use of membranes constituted by fibers with chemically active nanostructures, a procedure that substantially improves the removal capability. The most attractive characteristic of the use of membranes is that they can easily incorporate nanostructured active materials, while offering a high surface area per weight and easy conformity to almost all desired final shapes.

Among the different materials of this type proposed in the recent literature, it is possible to find membranes prepared with graphene or carbon nanotubes [23]. These carbon-based membranes are intended to substitute activated carbon, which is expensive to produce and difficult to regenerate. Yet, and in spite of the progress made in that regard, some hindrances to the more widespread use of these materials, mainly associated to limitations on their production and processability, still exist today.

Organic polymers are well suited to use in membrane fabrication due to their peculiar characteristics and very convenient properties, such as low cost, easy processability and exceptional mechanical resistance; also, the presence of a large number of functional groups may confer special properties to them, such as ionic exchange or superhydrophobic character [24]. In this way, polymeric membranes appear as one of the most promising materials for use in novel water treatment technologies. In recent years, some techniques to produce micro and nanostructured polymeric fibers have been reported. Among them, one can find melt blowing [24], multi-component fiber spinning [25] and electrospinning (ES) methods [26], with the latter deserving special attention for allowing the preparation of new types of materials that can be used in improved water remediation processes. ES is a low-cost, versatile and simple technique that can produce continuous polymeric fibers with diameters ranging from nanometers to a few micrometers, depending on the processing parameters to be adopted [26,27]. The membranes obtained through ES possess a combination of beneficial properties, such as high surface area-to-volume ratio, tunable pore sizes, high flexibility and good mechanical resistance, which makes them suitable materials for a wide range of applications. Most reports on the use of this technique for water treatment describe the preparation of membranes based on natural and synthetic polymers that present intrinsic functional groups capable of forming complexes with ionic species or metals [28]. However, alternative approaches have also been pursued, such as coating of the electrospun fibers, which is an attractive strategy that permits the integration of the nanostructures in a simple and cost-effective way [29–32], since a lesser amount of material is required for imparting the desired properties to the membrane. Also, with this methodology it is possible to create multifunctional materials capable of performing specific catalytic reactions, as interacting with the target pollutant and allowing its removal, or disinfecting the water body. Diverse materials have been investigated as agents to modify the fiber surface, including intrinsically conducting polymers (ICPs), whose peculiar physicochemical properties confer them a multifunctional character. ICPs have shown their potential for use as sensors [33], electromagnetic shielding [34] and energy storage materials [26], and more recently as affinity agents to extract pollutants [35] or highly valuable biomolecules [36]. PANI stands out among the ICPs due to its conductivity, electrochromism, chemical reactivity, stability, and simple and low cost synthesis [37]. More recently, several authors have made use of PANI (alone or in combination with other materials, as a manner of enhancing the performance) for the solid phase extraction of heavy metals and organic molecules, among other pollutants [22,36,38–40]. While high hydrophilicity in an acidic medium and good chemical activity are among the advantageous characteristics of this polymer for use in water treatment processes, there are still challenges to overcome with regard to the extent of its mechanical properties and stability (which limit the possibility of reusing the active material), and its lack of solubility in aqueous media or organic solvents (which prevent its processing by melting or drop casting methods, for instance) [41].

In this work, we describe the preparation of a new type of adsorbent material for use in water remediation processes, which is based on electrospun PS membranes with incorporated PANI chains on their surface. By following this strategy, we were able to bypass some of usual limitations found in previous PANI applications, since the NW PS membrane will work as a mechanically robust matrix that could be used in the most diverse water treatment setups. At the same time, the PANI chains incorporated as an additive on the surface of the PS template will function as a nanostructured layer that exhibits a vast number of active sites for adsorption of pollutants. In the present report, we also investigate the interfacial characteristics of the hybrid NW PS-PANI mat as an adsorbent material, by examining the isothermal adsorption curves of the CR dye. It is relevant to observe that our results reveal that a larger amount of CR dye is adsorbed when the conducting polymer is in its emeraldine base form (at a pH between 6.0 and 10.0). In previous reports, a better performance of PANI as an active adsorbent material is found to occur only at acidic media [39,42–44], which represents a possible limitation to a broader application of this polymer in water remediation processes.

2. Materials and methods

2.1. Materials

PS (MW of 280 kDa), CR (CI = 22,120) and ammonium persulfate (APS) were purchased from Sigma-Aldrich (USA). Dimethylformamide (DMF), aniline and hydrochloric acid (HCl) were provided by the Brazilian companies Vetec-Sigma, Nuclear and Química Moderna, respectively. All reagents were of analytical purity and used as received, except for aniline, which was distilled under reduced pressure before usage. In all experiments, we used deionized water obtained after passage through a Synergy ultrapure water purification system (Millipore, USA).

2.2. Preparation of nonwoven polystyrene-polyaniline mats

The NW PS mats were prepared using a homemade horizontal electrospinning system. First, we dissolved 2 g of PS in 10 mL of DMF and this solution was loaded in a plastic syringe with a stainless-steel spinneret 18 G (Beckton Dickinson, USA) and dispensed under a 17 kV voltage at a 0.5 mL/h rate by employing a NE-4000 syringe pump (New Era, USA). The fibers were collected on an aluminum foil attached to a grounded static metallic collector, dried at room temperature (25 °C) for 12 h, and then thermally and mechanically treated [41]. Subsequently, the mats were cut in 9 cm^2 squares and subjected to air plasma treatment using a PDC-002 plasma cleaner (Harrick, USA) during 5 min. We used an *in situ* chemical polymerization strategy to deposit the conducting polymer onto the pure NW PS mats. For this, the mats were placed in a beaker containing 0.52 mmol of aniline and 0.33 mmol of APS dissolved in 50 mL of HCl 1 M, and the reaction was allowed to occur

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