Kinetics and thermodynamic studies of Methyl Orange removal by polyvinylidene fluoride-PEDOT mats

Romário J. da Silva¹, Lizeth Carolina Mojica-Sánchez², Filipe D.S. Gorza¹, Graciela C. Pedro¹, Bruna G. Maciel¹, Gabriela P. Ratkovski², Hérica D. da Rocha¹, Kamila T.O. do Nascimento¹, Juan C. Medina-Llamas³, Alicia E. Chávez-Guajardo⁴, José J. Alcaraz-Espinoza⁵, Celso P. de Melo¹,2,*

¹Programa de Pós-Graduação em Ciência de Materiais, Universidade Federal de Pernambuco, 50670-901 Recife, PE, Brazil
²Departamento de Física, Universidade Federal de Pernambuco, 50670-901 Recife, PE, Brazil
³Centro de Estudios Científicos y Tecnológicos No.18, Instituto Politécnico Nacional, 98160 Zacatecas, Zac, Mexico
⁴Unidad Académica de Ciencias de la Tierra, Universidad Autónoma de Zacatecas, 98058 Zacatecas, Zac, Mexico
⁵Departamento de Química, Universidad Autónoma Metropolitana, 09340, Ciudad de México, México

A R T I C L E   I N F O

Article history:
Received 13 December 2019
Revised 21 April 2020
Accepted 21 April 2020
Available online 23 July 2020

Keywords:
Electrospinning
Composite mats
Pedot
Pvdf mats
Dye removal
Water remediation

A B S T R A C T

We report the preparation of poly(3,4-ethylene dioxythiophene) (PEDOT)-modified polyvinylidene fluoride electrospun fibers and their use as a novel adsorbent material for the removal of the anionic dye Methyl Orange (MO) from aqueous media. This novel adsorbent material can be used to selectively remove MO on a wide pH range (3.0–10.0), with a maximum capacity of 143.8 mg/g at pH 3.0. When used in a recirculating filtration system, the maximum absorption capacity was reached in a shorter time (20 min) than that observed for batch mode experiments (360 min). Based on the analyses of the kinetics and adsorption isotherm data, one can conclude that the predominant mechanism of interaction between the membrane and the dissolved dye molecules is electrostatic. Besides, considering the estimated values for the Gibbs energy, and entropy and enthalpy changes, it was established that the adsorption process is spontaneous and occurs in an endothermic manner. The good mechanical and environmental stability of these membranes allowed their use in at least 20 consecutive adsorption/desorption cycles, without significant loss of their characteristics. We suggest that the physical-chemical characteristics of PEDOT make these hybrid mats a promising adsorbent material for use in water remediation protocols and effluent treatment systems.

© 2020 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Introduction

Nowadays, access to a good water supply is a major social problem. In the past decades, water consumption at a global level increased at a faster rate than population growth. The produc-
tion of a large number of effluents contaminated by organic matter, heavy metal ions, hormones, dyes, and agrochemicals, among others, is inherent to many human activities, such as industries, mining, and agriculture. According to the World Health Organization (WHO), 2.1 billion people around the world did not have access to safe drinking water in 2017 (Organization, 2017). Each year, water contamination causes the death of 1.6 million people (Schwarzenbach et al., 2010), including more than 360,000 children (Organization, 2017).

In 1865, William Perkin revolutionized the food, textile, cosmetic, paper, leather, and paint industries by preparing the first synthetic organic dyes (Sharma et al., 2011). Since then, the large-scale use of synthetic dyes has made these compounds a recurring contaminant of industrial waters. Most of these chemical residues are stable under light exposure and environmental oxidation (Gong et al., 2013) and do not undergo biodegradation processes, remaining reactive during years.

Azo dyes, which represent the class of compounds most used in textile and food processes (Sharma et al., 2011) and account for 50%–70% of the world production of synthetic dyes (Gong et al., 2013), are characterized by the presence of one or more azo groups (–N=N–) attached to aromatic rings, substituted by different radical groups (Khanibadi et al., 2016). These compounds not only exhibit carcinogenic and mutagenic activity but also, even at low concentrations, can cause oxygen imbalance in aquatic environments, by impeding the penetration of the light necessary for plankton photosynthesis (Chang et al., 1994).

Methyl Orange (MO), an azo dye commonly used as a pH indicator in research laboratories, has found extensive application in the textile, printing, pharmaceutical, plastics, and food industry (Khanibadi et al., 2016). However, MO is an allergenic substance that can cause eczema upon contact with the skin (Khanibadi et al., 2016) and its presence in living organisms is considered harmful (Mittal et al., 2007). When present in the digestive system, MO can lead to a significant increase in the activity of the azo-nitro-reductase enzymes, producing aromatic amines that may cause intestinal cancer (Chang et al., 1994).

Even though MO does not possess a clear toxic qualification (Abdullah et al., 2012), the search for efficient remediation methodologies of this effluent remains of great relevance. The most common methods adopted include filtration, flocculation-coagulation, sedimentation, photodegrada-
tion, chemical oxidation, biological degradation, distilla-
tion, adsorption, and filtration (Nguyen and Juang, 2013; Robinson et al., 2001), each one of them facing its own limitations. While coagulation produces a large volume of tailings, chemical degradation (such as ozonation or Fenton’s reaction) may result in by-products that include very reactive organic molecules (Fu and Viraraghavan, 2001; Robinson et al., 2001) that may be toxic or carcinogenic (Nguyen and Juang, 2013; Robinson et al., 2001). Adsorption and filtration, two of the most used remediation methods (Sharma and Sanghi, 2012), present competitive advantages in terms of the required materials used as active agents with high dye removal capacities, low cost, good processability, high surface area, and possibility of recyclability (Dawood and Sen, 2014; Kyzas et al., 2013). Among the most commonly used adsorbents, polymeric membrane have attracted interest due to a superior efficiency in contaminant removal that can be associated to properties such as easy surface chemical modification and high surface area (Chen et al., 2020; Long et al., 2020; Teng et al., 2020). In addition, they can be used in practical systems of simple design and large operability (Gupta and Ali, 2013; Wang and Hsiao, 2016).

Both the type of the membrane adopted and the methodology selected to its production affect the efficiency and characteristics of the adsorption and filtration systems (Liao et al., 2018). Sintering, casting, layer-by-layer deposition (Gue et al., 2020), wet spinning, blow spinning, elongation, and phase inversion (Yu et al., 2020) are techniques commonly used for preparing polymer membranes, with the latter being the method most used in industry (Liao et al., 2018). In recent years, the electrospinning (ES) technique has been used to produce membranes of very different compositions and morphologies, with varied chemical-physical characteristics. Electrospun membranes (ESMs) are usually composed of a superposition of fibers with diameters that vary from a few tens of nanometers to a few micrometers, depending on the processing conditions and the nature of the materials used (Kumar et al., 2014). Effectively, ES is a simple and inexpensive technique to produce membranes with advantageous properties, such as a high surface area to volume ratio, adjustable porosity, high flexibility, and good mechanical resistance. Due to these characteristics, ESMs have been used in applications as diverse as energy storage (Ding, 2014), purification of biomolecules (Ma and Ramakrishna, 2008), biomolecule recognition and gas sensing (Merceante et al., 2017), controlled drug release (Mendes et al., 2016), tissue engineering (Ngadiman et al., 2017), energy conversion (Liu et al., 2018), catalysis (Formo et al., 2008), and environmental remediation (Focarete, 2018).

In the field of water remediation, it is possible to optimize the electrospun membranes based on different natural and synthetic polymers by incorporating functional materials selected for the capture of targeted contaminants (Wang and Hsiao, 2016). For instance, while Tian et al., 2011 used a cellulose ESM for the removal of mercury, copper, and cadmium ions. Gopi et al., 2017 reported that a polyvinylidene fluoride/chitosan (PVDF/chitosan) hybrid ESM had an adsorption capacity of 72 mg of the carmine indigo dye per gram, and Feng et al., 2018 used polyacrylonitrile and cellulose membranes to capture iron, copper and cadmium ions.

However, a widely used approach for the functionalization of ESM is their coating by the incorporation of nanostructures or other active agents (Focarete, 2018). This simple and effective strategy allows that a small amount of a properly chosen active material (e.g., nanotubes, graphene, nanoparticles, biomolecules, metal oxides, and polymers, among others) confer novel capture capabilities to the membrane. Due to their unique physical and chemical properties, the class of conductive polymers deserves special attention among the variety of materials that have been used to modify the surface of ESMs. Since their discovery in the mid-seventies, conducting polymers have found a broad range of applications, that include their use in sensor devices, electromagnetic shielding, organic electronics, mechanical actuators, and catalysis, among other fields (Das and Frasty, 2012). More recently, they have also been used as adsorbent materials for the treatment of effluents (Ibanez et al., 2018) and in the purification of biological molecules of high economic value, such as DNA (Maciel et al., 2018), proteins (Liu et al., 2006), amino acids (Zhou et al., 2019), and enzymes (Radovanić et al., 2016). Among these polymers, poly[3,4-ethylenedioxythiophene] (PEDOT) stands out for its high conductivity, biocompatibility, chemical stability, rapid and stable oxidation process, and the versatility of its synthetic routes (Liu, 2018). In recent literature, several authors have used PEDOT for the detection and removal of metal ions (Anandakumar et al., 2011; Checkol et al., 2018; Ahmad et al., 2015; Liu et al., 2018; Zuo et al., 2016), and the photocatalysis of antibiotics (Liu et al., 2019; Lu et al., 2018) and dyes (Katančić et al., 2018). To the best of our knowledge, there has been no report on the use of PEDOT for the direct adsorption and removal of dyes present in aqueous media. The low solubility and poor mechanical properties of this polymer are limiting factors to its more widespread in adsorption methodologies. As a manner to circumvent these problems, the present work describes the preparation of PEDOT modified polyvinylidene fluoride (PVDF) electrospun mats and their use.
as a novel adsorbent material for the removal of MO from aqueous media. PVDF, a chemically stable polymer that presents good mechanical properties, is widely used in the preparation of filter membranes. Here, PVDF fibers are adopted as mechanical support for the PEDOT chains (the active adsorbent material), so that the composite membranes can be used in varied configurations for efficient water treatment, both in filtering systems and in batch configurations.

1. Materials and methods

1.1. Materials

PVDF (MW of 530,000), 3,4-Ethylene dioxythiophene (EDOT), Methyl Orange (MO), sodium dodecyl sulfate (SDS), and iron (III) perchlorate hydrate (Fe(ClO₄)₂ · H₂O) were purchased from Sigma-Aldrich (United States). Acetone (ACT), dimethylformamide (DMF), methanol (CH₃OH), ethanol (C₂H₅OH), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were obtained from Química Moderna (Brazil). All reagents were of analytical grade and used as received. Deionized water (18 MΩ/cm) obtained after treatment with a Synergy ultrapure water purification system (Millipore, United States) was used in all experiments.

1.2. Preparation of nonwoven poly (vinylidene fluoride)-PEDOT mats

The nonwoven (NW) PVDF mats were prepared using a horizontal electrosprinning system equipped with a rotary collector. For this, initially, a solution of 17% (m/V) PVDF in DMF·ACT (2:3 ratio) was prepared under magnetic stirring at 60 °C for 6 h. Subsequently, this solution was introduced in a plastic syringe containing an 18 G stainless steel spinneret. Then, by employing a NE-4000 syringe pump (New Era, United States) a volume of 10 mL was dispensed under an 18 kV voltage at a 0.8 mL/hr rate atop an aluminum foil attached to a grounded 1200 r/min rotary collector. Finally, the NW PVDF mats so obtained were cut in 4 cm² squares and subjected to vapor phase polymerization for the deposition of the conductive polymer PEDOT on their surface. For this, a 150 μL of 0.2 mol/L Fe(ClO₄)₂ · H₂O methanol solution was deposited on the NW PVDF mats, and a waiting time of 20 min was allotted for evaporation of the solvent. Then, the mats were transferred to one support placed inside a desiccator, where a plate glass containing 40 μL of the EDOT monomer had been placed at its bottom. The desiccator was sealed and heated to 100 °C for 60 min to allow the polymerization to occur. After this, the mats were immersed four times for 30 min in ethanol to remove the oxidant in excess and finally stored in ultrapure water. The main steps of the mat preparation are shown in the scheme of Fig. 1. We carried out a polymerization kinetics study to establish the time required for the complete polymerization of the mats when a fixed amount of oxidant was deposited on the fibers.

1.3. Characterization methods

The chemical structure of the NW PVDF-PEDOT mats was investigated by infrared spectroscopy (FT-IR), using an IR tracer-100 spectrometer (Shimadzu, Japan) to collect the spectra of KBr pellet of the samples in the 4000 to 400 cm⁻¹ range. The morphological features and diameter of the fibers of the NW PVDF-PEDOT mats were assessed by SEM microscopy using a Mirar-3LM FEG microscope (TESSCAN, Czech Republic), with the homogeneity of the PEDOT coating investigated by Energy-Dispersive X-ray Spectroscopy (EDX). A BET analysis of the surface area and porosity of the PVDF and NW PVDF-PEDOT mats was performed by the use of a Gemini VII 2390 equipment (Micromeritics, United States). The processes of adsorption/desorption of MO on the NW PVDF-PEDOT mats were followed by using a UV-2600 spectrophotometer (Shimadzu, Japan) to collect the ultraviolet-visible (UV-Vis) absorption spectra of the dye solution before and after its interaction with the membranes.

1.4. Adsorption experiments

To establish the best conditions for the removal of MO, we varied a series of experimental parameters, such as the pH of the liquid medium, the interaction time, the initial concentration of dye, and the temperature. For this, we initially prepared a 300 mg/L stock solution of MO in ultrapure water. The pH was adjusted by the addition of small aliquots of 1 mol/L solutions of HCl and NaOH, as required. In these batch experiments, the NW PVDF-PEDOT mats were placed in a glass flask containing 20 mL of MO solutions with different concentrations, which was maintained at 160 r/min for different exposure times in the 5 to 720 min range. The wavelength of maximum absorption of MO varies with the pH of the medium. Hence, to assess the efficiency of the removal process, we measured the absorbance of the dye solution before and after the exposure to the NW PVDF-PEDOT mats, at 498 nm for pH < 4.0 and 464 nm for pH values in the 4.0 – 10.0 range. We first studied the influence of the pH of the medium in the 2.0–10.0 range, using an initial MO concentration of 20 mg/L and 120 min of interaction time. After establishing the optimal pH that corresponds to the maximum adsorption of the dye, we investigated the adsorption efficiency of the NW PVDF-PEDOT mats as a function of the initial MO concentration (1, 5, 10, 15, 20, 30, 40 mg/L), for interaction times varying in the (5–720) min interval. We expressed the efficiency of the MO adsorption by the NW PVDF-PEDOT mats as the percentage of adsorption, i.e.,

\[ \% \text{Ads} = \frac{C_0 - C_t}{C_0} \times 100\% \]  

where \(C_0\) (mg/L) is the concentration of the original MO solution and \(C_t\) (mg/L) is the dye concentration after the interaction with the NW PVDF-PEDOT mats. The adsorption capacity at time \(t\) (\(q_t\)) i.e., the amount in (mg) of MO adsorbed per mass unit (g) of PEDOT, was determined as

\[ q_t = \frac{V(C_0 - C_t)}{m} \]  

where \(V (L)\) is the volume of the solution, \(C_0\) (mg/L) is the initial concentration of the MO solution, \(C_t\) (mg/L) is the dye concentration in the solution at time \(t\), and \(m (g)\) is the mass of the PEDOT. After entering equilibrium, the adsorption capacity \(Q_e\), mg/g could be calculated as

\[ Q_e = \lim_{t \to \infty} q_t \]  

where \(C_e\) (mg/L) is the equilibrium concentration of dye solution (Gorza et al., 2018).

1.5. Thermodynamic experiments

For examining thermodynamic parameters as the corresponding Gibbs free energy \((\Delta G^\circ)\), enthalpy change \((\Delta H^\circ)\) and entropy change \((\Delta S^\circ)\), we initially placed the mats into a glass flask containing 20 mL of a MO solution with different initial concentrations (10, 15, 20, 30, 40 mg/L), which was then placed in bain-marie under a constant stirring of 160 r/min for 720 min. Subsequently, we allowed the samples to reach room temperature and then collected their UV–Vis absorption spectra. We carried out this analysis at different temperatures (10, 20, 30 and 50 °C).
1.6. Desorption and reusability experiments

For the desorption and reusability experiments, the NW PVDF-PEDOT mats were placed in a glass flask containing 20 mL of a 10 mg/L MO solution (pH 3.0) during 180 min and under a 160 r/min stirring. Then, the NW PVDF-PEDOT mats were transferred to a second flask containing 20 mL of 0.1 mol/L SDS aqueous solution, which was stirred for 60 min at 160 r/min to promote the dye desorption. Subsequently, aliquots of both the MO and SDS solutions were analyzed in a UV–Vis spectrophotometer to determine the corresponding levels of adsorption and desorption. Finally, the NW PVDF-PEDOT mats were washed extensively with ultrapure water and reused in a new adsorption/desorption cycle, in a process that was repeated for a total of 20 consecutive times.

1.7. Dye-Water filtration experiments

We also explored the use of the NW PVDF-PEDOT mats as active filtering materials when the dye solution was recirculated in a closed configuration. In these experiments, the MO solution was maintained in a constant flow perpendicularly directed to the surface of the mats. For this, six circular mats (diameter of 19 mm) were stacked and accommodated in one support, as schematically shown in Appendix A Fig. SI-1. We used 100 mL of a 10 mg/L MO solution in a flow of 200 mL/min in a closed system. The kinetics of adsorption in the removal process was monitored by periodically taking aliquots of the solution for analysis by UV–Vis spectroscopy. For future comparison with the batch mode kinetics, in these experiments, we maintained fixed the relationship between the mass of the adsorbent and the dye volume used in batch mode.

1.8. Selectivity experiments

The selectivity of the mats for adsorbing MO relative to other dyes was also examined. For this, we used a mixed aqueous solution of MO with a second dye (methylene blue, toluidine blue, Rhodamine B, Congo red and indigo carmine), with a 1:1 molar ratio. We adopted a similar condition (pH 6.0, a concentration of 10 mg/L and a volume of 10 mL) for all initial binary dye solutions. We placed the mixed solutions into a 50 mL glass flask containing one mat, which was stirred at 160 r/min for 12 hr. UV–Vis spectra were taken of aliquots of the solutions collected before and after their exposure to the mats.

2. Results and discussion

2.1. Characterization of nonwoven poly(vinylidene fluoride)-PEDOT mats

We performed an FT-IR analysis of both pristine PVDF and NW PVDF-PEDOT mats to investigate the process of formation of the PEDOT layer on the surface of PVDF mats (Fig. 2). The absorption peaks of the pristine PVDF polymer were identified at (a) 1675 and 1406 cm⁻¹, which were assigned to the C = C and C–F stretching vibrations, respectively (Lanceros-Méndez et al., 2001; Zeng et al., 2016), (b) at 880 cm⁻¹, which was related to the vinylidene group (−C = CH₂) (Peng and Wu, 2004; Zeng et al., 2016), and (c) at 1071 and 831 cm⁻¹, which were associated to the crystalline and amorphous phases of PVDF (Zeng et al., 2016). In the NW PVDF-PEDOT mats spectrum, the successful PEDOT polymerization could be confirmed by the identification of the peaks related to the asymmetric [symmetric] stretching mode of C = C at 1517 cm⁻¹ (around 1385 cm⁻¹), and to the stretching vibrations of the C-S-C bond of the thiophene ring around 980 and 688 cm⁻¹ (Kang et al., 2013; Xie et al., 2016).

In Fig. 3, we present the SEM images of the pristine PVDF membrane and the NW PVDF-PEDOT mats. By examining the PVDF membrane before the PEDOT deposition (Fig. 3a and c), one can observe that the surface of PVDF fibers is very sensitive to the parameters of the ES process and exhibits a broad size distribution. The average diameter of the fibers of the pristine PVDF mats is of the order of 250 nm (inset of Fig. 3). The deposited PEDOT layers modify the surface of the PVDF fibers (Figs. 3b and d). In the EDX elemental maps for C, F, S, and Cl showed in Appendix A Fig. SI-2, one can observe that the NW PVDF-PEDOT mats present a uniform distribution of the different elements along the fibers; specifically, the presence of sulfur indicates that the polymerization of the EDOT monomers occurs over the entire fiber surface. Also, the EDX pattern shown in Appendix A Fig. SI-3 confirms the presence of the previously mentioned elements.
Fig. 2 – Infrared spectra of (a) pristine PVDF and (b) NW PVDF-PEDOT mats.

Fig. 3 – SEM micrographics of pristine PVDF (a) and (c); NW PVDF-PEDOT mats (b) and (d) at different magnifications.
Table 1 - BET surface and pore parameters for PVDF and NW PVDF-PEDOT mats.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g) (BET method)</th>
<th>Pore volume (cm³/g) (BJH method)</th>
<th>Pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>4.412 ± 0.126</td>
<td>0.0012</td>
<td>19.57</td>
</tr>
<tr>
<td>PVDF-PEDOT</td>
<td>5.691 ± 0.118</td>
<td>0.0007</td>
<td>18.07</td>
</tr>
</tbody>
</table>

For the determination of the surface area of the PVDF and NW PVDF-PEDOT membranes, we adjusted the data of the adsorption of N₂ at 77 K to the BET model (Table 1), with corresponding correlation coefficients (R²) higher than 0.98. These results reveal an enhancement of the surface area after the deposition of the PEDOT layer, in concordance with the presence of nanograins as observed in SEM images (Fig. 3). Furthermore, the micropore diameter (~20 Å) exhibited a slight decrease after the PEDOT layer deposition.

Also, both the wettability characteristics (Appendix A Fig. SI–4) and the studies of PEDOT polymerization kinetics (Appendix A Fig. SI–5) corroborated the information collected from the micrographs and FT-IR spectra, proving the incorporation of PEDOT on the surface of PVDF mats. Moreover, the comparison of the UV–Vis spectrum (Appendix A Fig. SI–6) of the pristine PVDF and NW PVDF-PEDOT mats reveals in the latter the large absorption in the near-infrared region characteristic of the presence of polaron and bipolarons, indicating that PEDOT is in its conductive form.

2.2. Adsorption experiments and adsorption mechanism

In a first experiment, we monitored the adsorption process by collecting the MO dye absorption spectrum in the visible region, before and after interaction of the dye with the NW PVDF–PEDOT mats and a pristine PVDF membrane. In Appendix A Fig. SI–7, we show the UV–Vis spectra corresponding to an adsorption process that lasted 2 hr. While it is possible to observe a noticeable decrease of the MO band absorption (ν→π* transition) (Masoud and Hammud, 2001) after the interaction with NW PVDF–PEDOT mats, almost no change occurs in the case of the PVDF membrane, confirming that the pristine PVDF membranes do not adsorb the dye.

The pH of the medium may affect not only the surface charge of the adsorbent but also the degree of ionization and the structure of the dissolved dye molecules. Hence, for investigating the dominant adsorption mechanisms, it is important to perform an analysis of how the adsorption efficiency varies with the pH. These experiments were carried using a solution of KCl 0.1 mol/L and varying the pH with HCl 1 mol/L and NaOH 1 mol/L, with the NW PVDF–PEDOT mats allowed to interact for 24 hr. We have found that the zero charge point (pHₚzc) of the NW PVDF–PEDOT mats is close to 5.3, as shown in Fig. 4a.

While the surface of NW PVDF-PEDOT mats is positively charged in an acidic media, it exhibits a slightly negative charge at other pH values. Within the range of initial pH investigated, we observed a relatively narrow variation (∆pH) of the pH value of the KCl solutions after 24 hr of immersion of the mats (Bakatula et al., 2018) (Fig. 4a). This fact can be associated with the oxidation of the PEDOT chains in acidic medium, which results in the creation of positively charged polarons and bipolarons. During the EDOT polymerization, Fe(ClO₄)₂ was used as the oxidant, and so the (ClO₄)⁻ ions present can act as counterions of the oxidized (i.e., positively charged) PEDOT chains. However, the oxidation degree changes when one uses a NaOH solution to adjust the pH of the medium, due to the transformation of bipolarons in polarons, and of polarons in neutral PEDOT segments (Khan et al., 2015). Then, the final pH slightly decreases, due to the OH⁻ consumption by the ionic exchange between (ClO₄)⁻ and OH⁻ ions in the PEDOT chains (Tehrani et al., 2007), in a process that can be followed by UV–Vis spectroscopy (Appendix A Fig. SI–12).

The effect of the pH variation on the adsorption process can be seen in Fig. 4b. At pH 2.0, the MO removal degree is reduced to 42%, because of the more limited interaction of the dye molecules with the membrane surface. As one can observe in Fig. 5b, the adsorption process is not favored in a very acidic medium, when the MO dye becomes positively charged due to the protonation of the nitrogen atoms. Since the pKa of MO is 3.39, the dye molecules become negatively charged around pH 3.9, the electrostatic interaction is now favored, and the removal efficiency increases to 75%. For this reason, a value of pH = 3.0 was adopted in the subsequent studies. The rate of adsorption, which remains essentially the same until the neutral pH, slightly decreases (to a 65% level) at alkaline media, when the surface of the membranes turns slightly negative. One can attribute the process of adsorption of the MO molecules onto the NW PVDF–PEDOT mats to the electrostatic interaction between the SO₃⁻ group of the dye molecule and the charged polaron and bipolaron defects present in the PEDOT chains, as depicted in Fig. 5a. For this to occur, ionic exchanges must exist between the (ClO₄)⁻ counterions distributed along the polymeric chains and the dye SO₃⁻ groups. It is indeed known that one can use molecules (such as polystyrene sulfonate and dimethyl sulfoxide) that contain the sulfonic group as coun-

Fig. 4 – (a) Determination of the point of zero-charge pHₚzc and (b) effect of pH variation on the removal rate of MO dye by the NW PVDF–PEDOT mats.
terions and dopants of the PEDOT chains (Chou et al., 2015; Elschner et al., 2010).

2.3. Adsorption process

The adsorption capacity of the NW PVDF-PEDOT mats would be affected by the time allowed for the adsorbent/adsorbate interaction and the initial MO concentration. To examine this, room temperature experiments were performed at pH = 3.0, for initial dye concentrations varying in the (1–40) mg/L range. In Fig. 6a, we present the data relative to the removal of the dye for different contact times with the NW PVDF-PEDOT mats and varying initial MO concentrations (1, 5, 10, 15, 20, 30, and 40 mg/L). One can observe that the removal rate is higher (70%) and occurs more rapidly (60 min) at the lowest concentrations used (1, 5, and 10 mg/L). At a higher concentration (40 mg/L), the percentage of removal is substantially lower (20%), but a faster rate of adsorption is observed. Hence, the higher the initial MO concentration, the more rapidly will the system reach the adsorption equilibrium. Since the interaction is mainly electrostatic, a limited number of charged MO molecules can approach and interact with the membrane surface. At lower concentrations, saturation occurs, with the physiochemical equilibrium being reached in 360 min. On the other hand, a faster (60 min) saturation is observed at higher concentrations, due to the higher amount of dissolved dye molecules.

As one can observe in Fig. 6b, the removal efficiency decreases as the initial concentration increases, and the adsorption capacity of NW PVDF-PEDOT mats reaches its maximum value (143.8 mg/g) at the concentration of 20 mg/L. One can attribute this increase in the adsorption capacity to the higher number of dye molecules that become available to interact with the active PEDOT sites. In turn, this favors the motive force of mass transfer between phases, favoring the adsorption process (Gorza et al., 2018).

2.4. Effect of the temperature

To evaluate the effect of the temperature upon the removal capacity of the NW PVDF-PEDOT mats, batch adsorption experiments were carried out at different temperatures in the (283–323) K range for initial MO concentrations varying between 1 mg/L and 40 mg/L. As the results of Fig. 7 indicate, the adsorption capacity $Q_e$ significantly increases with the temperature (from 143.8 mg/g at 283 K, to 293 mg/g, at 323 K). The decrease of the viscosity of the solution (Xie et al., 2016) favors the interaction of the dye molecules with the membrane.
Table 2 – Kinetics parameters for MO adsorption by the NW PVDF-PEDOT mats.

<table>
<thead>
<tr>
<th></th>
<th>Qe, exp (mg/g)</th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
<th>Morris-Weber</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>k1 (hr⁻¹)</td>
<td>Qe, calc (mg/g)</td>
<td>k2 (g/mg.hr)</td>
</tr>
<tr>
<td>233 K</td>
<td>143.864</td>
<td>0.692</td>
<td>84.043</td>
<td>0.927</td>
</tr>
</tbody>
</table>

Fig. 7 – Effect of temperature on the adsorption process of MO dye by NW PVDF-PEDOT mats.

2.5. Adsorption kinetics

We investigated the nature of the mechanisms prevailing in the interaction of the MO molecules with the NW PVDF-PEDOT mats, by adjusting the data of experiments carried out at 293 K and pH 3.0, for an initial dye concentration of 40 mg/L, to different kinetics models (Appendix A Fig. SI-8). We used the linearized expressions of the pseudo-first-order (PFO), pseudo-second-order (PSO), and Morris-Weber models, given respectively by Eqs. (4–6) (Gorza et al., 2018)

\[
\ln (Q_e - q_t) = \ln (Q_e) - k_1 t 
\]

\[
\frac{t}{Q_e} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} 
\]

\[
q_t = k_d t^{0.5} + C 
\]

where Qe (mg/g) and q (mg/g) were the amounts of MO molecules adsorbed at equilibrium and at time t (min), respectively, and k1 (k2 (min⁻¹)) is the adsorption rate constant for the pseudo-first (pseudo-second) model, and k_d and C are the adsorption rate (min⁻¹) and intraparticle diffusion constant (Morris-Weber), respectively. The linear regression method was used to determine the kinetics parameters k1, k2, k_d, and C are the correlation coefficients (R²) and the Qe,calc values (Table 2). As the data of Table 2 reveal, the adsorption process is better described by the PSO model, for which we obtain an R² of 0.999 and an estimated Qe,calc of 149.7 mg/g, which is very close to the experimentally determined value (Qe,exp = 143.8 mg/g). Hence, the dominant adsorption mechanism is chemical.

Table 3 – Langmuir and Freundlich isotherm parameters for MO adsorption onto NW PVDF-PEDOT mats.

<table>
<thead>
<tr>
<th></th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>q_m (mg/g)</td>
<td>K_L (L/mg)</td>
</tr>
<tr>
<td></td>
<td>146.194</td>
<td>1.378</td>
</tr>
</tbody>
</table>

2.6. Adsorption isotherms

The fitting of the adsorption data to standard isotherm models is an additional tool for understanding the nature of the process governing the adsorbent/adsorbate interaction. Hence, the corresponding experimental data were adjusted to the Langmuir and Freundlich models. The Langmuir isotherm model describes adsorption processes in which a finite number of energetically identical sites capture a single molecule per site, resulting in the formation of an adsorbate monolayer atop the surface of the adsorbent (Foo and Hameed, 2010). It can be expressed in its linear form as

\[
\frac{C_e}{Q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} (7)
\]

where C_e (mg/L) is the adsorbate concentration in the equilibrium, Q_e (mg/g) is the amount of the adsorbate adsorbed per mass unit of the adsorbent, q_m (mg/g) is the maximum adsorption capacity and K_L (L/mg) is the adsorption equilibrium constant. We determined the values of q_m and K_L by adjusting the data to the C_e/Q_e vs. C_e curves (Appendix A Fig. SI-9a).

On the other hand, the Freundlich isotherm model can be applied to non-ideal systems in which the capturing sites are energetically heterogeneous, causing the adsorption to occur in multilayers since the more energetic sites can interact with more than one molecule of the adsorbate (Foo and Hameed, 2010). In its linear form, one can write

\[
\log Q_e = \log K_f + \frac{1}{n} \log C_e (8)
\]

where K_f (mg¹⁻¹/L⁻¹/ₙ) (g⁻¹ 1/ₙ) and n are the constants related to the adsorption capacity and the heterogeneity of surface, respectively. The values of these parameters were estimated by fitting the experimental data to logQ_e vs. logC_e curves (Appendix A Fig. SI-9b).

The experimental data were fitted according to two isotherm models (Appendix A Fig. SI-10). From the data presented in Table 3, where we summarize the results of the two types of fitting, one can see that the Langmuir isotherm model provides for a higher correlation coefficient (R² ≥ 0.99) and an adsorption capacity (q_m = 146.194 mg/g) closer to the experimental value (143.8 mg/g). Hence, the adsorption of the MO dye onto NW PVDF-PEDOT mats should occur with the formation of a monolayer, with each one of the available adsorption sites capturing a single dye molecule interacting (Chávez-
Table 4 – Thermodynamic parameters for MO adsorption onto NW PVDF-PEDOT mats.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>ΔG° (kJ/mol)</th>
<th>ΔH° (kJ/mol)</th>
<th>ΔS° (kJ/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>-27.872</td>
<td>4.123</td>
<td>0.1123</td>
</tr>
<tr>
<td>293</td>
<td>-28.952</td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>-30.088</td>
<td></td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>-32.381</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Gujardo et al., 2015. This hypothesis is consistent with the results of previous studies on MO adsorption using polypyrrole (Boukoussa et al., 2018) and activated carbon (Pal et al., 2013).

2.7. Thermodynamic analysis

To assess the effect of temperature upon the process of adsorption of the MO molecules onto the surface of the NW PVDF-PEDOT mats, one can estimate the values of the thermodynamic parameters Gibbs free energy (ΔG°), and the enthalpy change (ΔH°) and entropy change (ΔS°). We used the relationships

\[ \Delta G° = -RT \ln (K_L) \]  

(9) and

\[ \ln K_L = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \]  

(10)

where \( K_L \) is the Langmuir equilibrium constant at different temperatures, \( R \) is the universal gas constant, and \( T \) (K) is the temperature in which the adsorption data were collected. With this, it is possible to determine not only whether the adsorption occurs in an endothermic or exothermic manner, but also if the process is spontaneous or not.

While ΔG° can be directly determined from Eq. (9), ΔH° and ΔS° were calculated by determining the intercept and slope of the Van’t Hoff plots of ln(KL) versus 1/T (Appendix A Fig. SI-11). In Table 4, we summarized the values of the thermodynamic parameters at different temperatures. The negative values of ΔG° suggest that the adsorption process of MO onto the surface of NW PVDF-PEDOT mats is spontaneous and thermodynamically favorable. When the temperature is increased, the magnitude of ΔG° becomes more negative, indicating that the adsorption process is favored (Umpuch and Sakaew, 2013).

For the case of adsorption processes (Unnithan and Anirudhan, 2001), a ΔG° value in the range -20 to 0 kJ/mol corresponds to a spontaneous physical mechanism, while a value between -80 to -40 kJ/mol indicates the occurrence of chemisorption. Also, the positive value of ΔH° (4.12 kJ/mol) indicates that the adsorption process is endothermic, a hypothesis supported by the increment in the adsorption of the MO molecules with the temperature increase. Finally, the positive value of ΔS° (0.112 kJ/mol K) suggests an increase in the randomness of the capture process at the adsorbent-solution interface.

2.8. Desorption and reusability experiments

By adopting the conditions described in Section 1.6, 20 consecutive adsorption/desorption cycles were performed to test the reusability of the NW PVDF-PEDOT mats. As the corresponding data show (Fig. 8), the NW PVDF-PEDOT mats exhibit their maximum capacity of removal, close to a 100% level of adsorption, when first exposed to the contaminants. However, only a little over 80% of the deposited material desorbs when the mats are immersed in the eluent SDS solution. The subsequent adsorption/desorption rates remain constant at 70% (adsorption) and > 95% (desorption). These facts can be rationalized if one considers that upon the first exposure of a mat to the contaminants, some dye molecules adsorb to innermost sites of the membrane, which are not readily accessible to SDS molecules of the eluent solution. Thus, the desorption efficiency is low in the 1st cycle. The presence of these incorporated dye molecules accounts for the observed reduction in the adsorption rate in the subsequent cycles. The newly adsorbed molecules of the contaminant are now in sites easily accessible to the SDS solution, and hence desorption close to 100% occurs at each new elution step, confirming that the NW PVDF-PEDOT mats have optimum chemical stability. No significant loss in their removal efficiency was observed during at least 20 repeated adsorption/desorption cycles.

The capture of the dye by the NW PVDF-PEDOT mats can be described as resulting from the exchange of the counterions, which counterbalance the polaron and bipolaron defects along the PEDOT chains, by the SO₃⁻ groups of the MO molecules. In the desorption process, the dye is substituted by the SDS molecules used in the cleansing step.

2.9. Filtration experiments

Batch mode experiments and filtering systems are the most used procedures for the removal of contaminants from an aqueous medium. Naturally, the lifecycle of the membrane used as an active adsorption agent depends on the configuration adopted. The chemical composition, porosity, and mechanical resistance, among others, are relevant parameters for determining the efficiency of a membrane.

We examined the performance of the NW PVDF-PEDOT mats when used in a dead-end filtering configuration. For this, six stacked circular mats (diameter of 19 mm) were positioned on one fixed support perpendicularly to a constant 200 mL/min flow of a 10 mg/L MO aqueous solution (Appendix A Fig. SI-1). We used identical values of the MO concentration (10 mg/L) and pH (3.0) for experiments in batch and filtering configurations. The evolution of the removal percentage is quite similar in both cases, as one can observe from the data shown in Fig. 9. However, while in the filtration system saturation was reached within 20 min, 360 min were required in the batch mode case. Hence, the adsorption rate is at least 18 times higher in a filtering configuration than when NW PVDF-PEDOT mats are used in a batch mode.

The significant increment of the removal rate observed in the recirculation experiments could be expected since, in this
configuration, the MO solution is repeatedly forced to traverse the NW PVDF-PEDOT mats. Hence, more effective interaction of the dye molecules with the active sites in the interior of the membrane becomes favored (Gorza et al., 2018).

2.10. Selectivity experiments

At low pH values, the PEDOT chains become positively charged (with the presence of polaron and bipolaron defects), favoring the adsorption of anionic dyes. As discussed in Section 1.2, the NW PVDF-PEDOT mats capture the MO molecules mainly due to the electrostatic interaction between the S-H⁺ groups of the conducting polymer and the sulfonic (SO₃⁻) terminal ends of the dye.

To examine this question further, we carried out experiments for testing the selectivity of the NW PVDF-PEDOT mats towards cationic and anionic dyes. For this, a series of removal tests were performed using binary mixtures of MO and the dyes CR (Congo Red) and IC (Indigo Carmine), which have anionic character, and MB (Methyl Blue), RB (Rhodamine B) and TB (Toluidine Blue), of cationic nature. The efficiency of the removal process could be estimated by the absorbance spectra of the liquid medium after a 12 hr exposure to an immersed membrane. As could be expected, the selectivity towards anionic is confirmed. The corresponding results (Fig. 10) indicate that while in the case of binary mixtures with cationic dyes a marked decrease is observed solely in the intensity of the band centered in 460 nm (the characteristic MO absorption band), the NW PVDF-PEDOT mats can remove both dyes in the case of the MO-CR and MO-IC binary solutions. In all cases (see insets of Fig. 10), the effectiveness of the dye removal can be visually followed by the noticeable change in the color of the binary solution.

2.11. Comparative studies on the Mo MO adsorption efficiency

A comparison of the performance of the NW PVDF-PEDOT mats with other materials reported in the literature is shown in Appendix A Table S1.1. We point out that the main comparative advantages of using the NW PVDF-PEDOT mats reside in a shorter time (60 min) required for effective interaction and a higher degree of desorption (> 97%). Also, they exhibit a larger operational lifespan under repeated adsorption/desorption cycles. During the reusability studies, the NW PVDF-PEDOT mats maintained their adsorptive properties substantially unaltered for at least 20 cycles, and this operational limit is likely to be further extended. The capacity of adsorption of the NW PVDF-PEDOT mats (Qₑ = 143.8 mg/g) is in the intermediate range when compared to those of metal oxide-based materials – such as the ones reported: 381 mg/g (Arshadi et al., 2021).
Fig. 9 – Comparison between different configuration systems using filtration mode and batch mode to the removal of MO by the NW PVDF-PEDOT mats.

3. Conclusion

This work has explored a simple methodology for obtaining NW PVDF-PEDOT composite mats, in which the conducting polymer is incorporated in situ on a PVDF matrix previously produced by electrospinning methods. The fibers of these electrospun PVDF membranes presented an average diameter of 0.9 ± 0.7 μm and sizes in the 100 nm to 2 μm range. The NW PVDF-PEDOT mats can be used to remove the anionic dye MO on a wide pH range 3.0 – 10.0, with a maximum capacity of 143.8 mg/g at pH 3.0. Based on kinetics, adsorption, and thermodynamics analyses, it could be inferred that the predominant mechanism of interaction between the membrane and the dissolved dye molecules is electrostatic, and a spontaneous character. The NW PVDF-PEDOT membranes were environmentally stable and maintained their mechanical characteristics during at least 20 consecutive adsorption/desorption cycles. When used in a recirculating filtration system, their maximum absorption capacity was reached in a much shorter time (20 min) than that observed in batch mode (360 min). We believe that the present results can provide an initial guideline for subsequent work devoted to the optimization of the physical-chemical characteristics of PEDOT-based adsorbent materials for their effective use in water remediation protocols and efficient treatment systems.

Acknowledgement

This work was supported by the Brazilian agencies CNPq, FUNASA, FACEPE, INFO Institute, and ELINOR Nanobiotechnology network. RJS thanks CNPq for a Ph.D. fellowship. JCML and AECG acknowledge the financial support from the Mexican agency CONACyT. The authors thank Professor H. P. de Oliveira (UNIVASF) for the BET measurement and analysis.

Appendix A Supplementary data


REFERENCES


Gong, R., Ye, J., Dui, W., Yan, X., Hu, J., Hu, X., et al., 2013. Adsorptive Removal of Methyl Orange and Methylene Blue from Aqueous Solution with...


