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Green reduced graphene oxide incorporated into polyacrylonitrile membranes for multi-component removal from water

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Abstract

Organic contaminants are hardly treated by the conventional water treatment. Advanced treatments, as adsorption and filtration, are highlighted by their excellent removal capacity. To this proposal, reduced graphene oxide (rGO-G) was produced by a green route with carrot extract, and it was incorporated into polyacrylonitrile membranes. This material was characterized and applied in emerging contaminants removal. The membrane with 7.5% of rGO-G showed excellent adsorption of ciprofloxacin (CPX), levofloxacin (LVX), and moxifloxacin (MFX), with adsorption capacity of 20 mg/g, 9.8 mg/g, and 16.5 mg/g, respectively. The membrane showed an increase in adsorption capacity of 158.4% and 83.3% for CPX and MFX, respectively when compared to the pristine membrane of polyacrylonitrile. Also, the membrane incorporating 5% of rGO-G showed the best performance for acetaminophen (ACMP), atrazine (ATZN), and sulfamethoxazole (SMTX), with removal of 62%, 59%, and 68%. The filtration was studied by FTIR and XPS, which indicated the mechanism as $\pi - \pi$ and hydrogen bonds interaction.

Keywords: green route; polymeric membrane; emergin contamiannt; adsorption; nanofiltration.

1. Introduction

Emerging contaminants (EC), as pharmaceuticals, surfactants, and pesticides, are highly applied in industrial and agricultural activities. The ECs are complex, widely consumed, harmful to the environment, can be bioaccumulated, and cause bacterial resistance [1].

The complexity of these chemicals intensified the necessity of advanced technologies for water treatment, as adsorption and nanofiltration. To this proposal, the reduced graphene oxide (rGO) stands as an interesting material due to the possibility of $\pi - \pi$ interactions and hydrogen bonds [2]. To immobilize the powder rGO, polymeric membranes, as polyacrylonitrile (PAN), have been reported by the stability, and anti-fouling properties [3].

Thus, this project aimed to produced rGO by a green route as an alternative to the conventional methods with hydrazine, and to incorporate this material into PAN membranes at different concentrations. These membranes were characterized and applied in emerging contaminants removal in adsorption and nanofiltration experiments.

2. Methods

2.1. Reduced graphene oxide production

Graphene oxide (GO) was produced by the modified methodology of Prediger et al. [4], as the protocol described by Hummers [5]. The GO was applied in the rGO production by a green route with carrot extract [6]. The carrots were peeled, washed, and placed in a reaction flask with ultrapure water, under reflux for 24 h. The carrot extract was mixed with GO, and subjected to reflux under 7 days, resulting in the green rGO (rGO-G).

2.2. Production of the polyacrylonitrile membrane with green reduced graphene oxide

PAN, lithium chloride, dimethylformamide were mixed in a reaction flask, under magnetic stirring at 60 °C. Aiming at the production of PAN membrane with rGO-G, rGO-G was added into the PAN suspension at concentrations of 2.5%, 5%, and 7.5%. After the suspension reach room temperature, 1 mL was placed into a petri dish and submerged in ultrapure water. The formed membranes were hydrolyzed in NaOH solutions (1,5 M, 45 °C, and 90 min). The membranes were named as hPAN@rGO-G1, hPAN@rGO-G2, and hPAN@rGO-G3. The materials were characterized by their morphology and physicochemical aspects.

3.3. Adsorption experiments

A 1 cm^2 square membrane was placed into a beaker with 5 mL of contaminants solution containing ciprofloxacin (CPX), levofloxacin (LVX), and moxifloxacin (MFX) at 10 mg/L, at room temperature. The system was stirred a orbital shaker for 24 h.

3.4. Membrane filtration

A feed pump was applied to maintain the flux of the multi-component solution of the emerging contaminants: acetaminophen (ACMP), atrazine (ATZN), and sulfamethoxazole (SMTX) at 1 mg/L. The concentration of the contaminant was analyzed by HPLC.

3. Results and discussion

3.1. Materials characterization

The GO reduction was confirmed by XRD patterns, and the interlayer spacing was of 0.38 nm, confirming the reduction [4]. The FTIR analysis of rGO showed the presence of O–H, C=O, C=C, and C–O groups, as reported for this carbon-based material [4]. XPS analysis of rGO showed the presence of carbon (78.3%), oxygen (17.8%), and nitrogen (2.9%). Zeta potential of rGO-G was around –10 mV in all pH analyzed (4-10).

The FTIR spectra of the hPAN@rGO-G membranes showed the presence of O–H, C–H, and C≡N groups. It was also suggested that H-bonds occurred between hPAN and rGO-G. XPS analyses indicated that the increment of rGO-G caused an increase in C/O rate, indicating an increase in carbon domain. Zeta potential analyses showed that rGO-G incorporation caused an increased in the surface charge (the membrane became less negative).

The membranes were also analyzed by water contact angle, indicating that the membrane became more hydrophobic according to the rGO-G increment. The pure water flux was also analyzed, and it increased with the increment of rGO-G in the membrane.

The morphology of the membranes was analyzed by AFM (Fig 1a-d). The hPAN membrane (Fig 1a) had a smooth surface, which become rougher with the increment of rGO-G. The membrane hPAN@rGO-G1, hPAN@rGO-G2, and hPAN@rGO-G3 had a roughness of 45 nm, 62 nm, and 76 nm, respectively. The wight spots in the membrane surface might be associated with the presence of rGO-G.

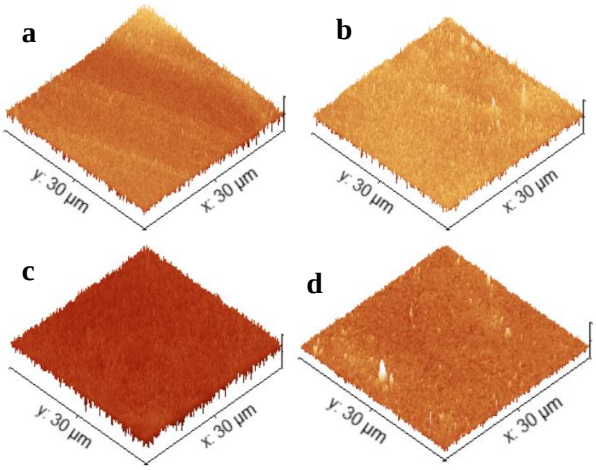

Fig. 1. AFM images: (a) hPAN; (b) hPAN@rGO-G1; (c) hPAN@rGO-G2; (d) hPAN@rGO-G3.

The membranes were also evaluated by SEM (Fig 2a-d). It was observed the presence of a finger-like sublayer through the cross-section, in which the macrovoids became thinner with the increment of rGO-G in the membranes. Also, the thickness of the membranes was similar, as common happens to one-layer membranes [7].

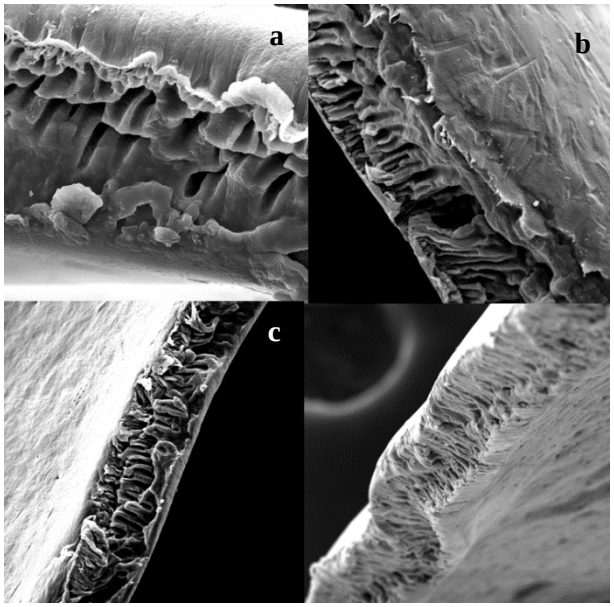

Fig. 2. SEM images: (a) hPAN; (b) hPAN@rGO-G1; (c) hPAN@rGO-G2; (d) hPAN@rGO-G3.

3.2. Adsorption experiments

The adsorption experiments were performed with the membrane hPAN@rGO-G3, which had the highest roughness. It was previously studied that higher roughness can improve adsorption by the increase in the active sites in the material surface [8]. The removal of CPX, LVX, and MFX by the hPAN@rGO-G3 was assessed by batch experiments (Fig 3). The adsorption capacity of hPAN@rGO-G3 was 20 mg/g, 9.8 mg/g, and 16.5 mg/g for CPX, LVX, and MFX, respectively. The presence of rGO-G caused an increase in the material adsorption capacity in 158.4% and 83.3% for CPX and MFX, respectively. The pristine membrane of hPAN was not capable of removing LVX, but the presence of rGO-G caused an adsorption capacity of 9.8 mg/g. These results showed a direct relation between the adsorption capacity and the presence of rGO-G. It probably happened due the presence of $\pi - \pi$ interactions between aromatic rings from rGO-G and the antibiotics, hydrogen bonds and electrostatic interactions between protonate amides of the contaminants and the negative material.

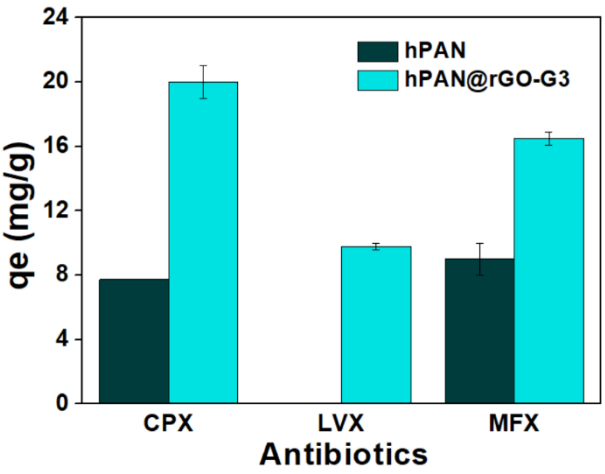

Fig. 3. Adsorption experiments with ciprofloxacin, levofloxacin, moxifloxacin. Antibiotics concentration of 10 mg/L, membrane mass of 0.0025 g, volume of 5 mL, 25 °C, pH 6, and 24 h.

3.3. Filtration experiments

The filtration experiments were carried out with the hPAN@rGO-G2 membrane, since it had intermediate roughness, and hydrophilicity. The removal of for ACMP, ATZN, and SMTX in a multi-component solution was 62%, 59%, and 68%, respectively (Fig 4). The filtration mechanism was studied by FTIR and XPS, confirming the presence of hydrogen bonds and electrostatic interactions (Fig 5) between NH/OH functions of the ECs and carboxyl/hydroxyl groups from the hPAN@rGO-G2 membrane.

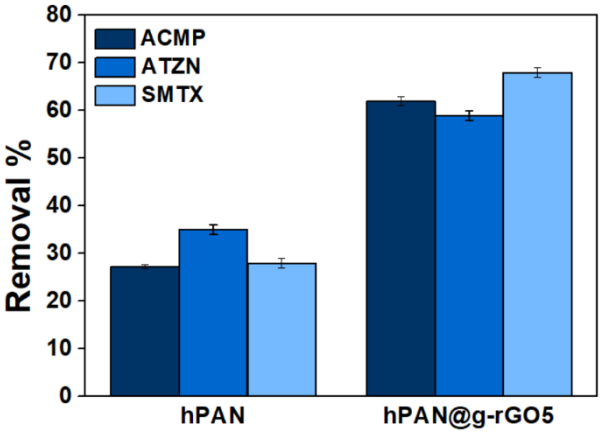

Fig. 4. Filtration experiments in multi-component. Contaminants concentration of 1 mg/L and pH 6.

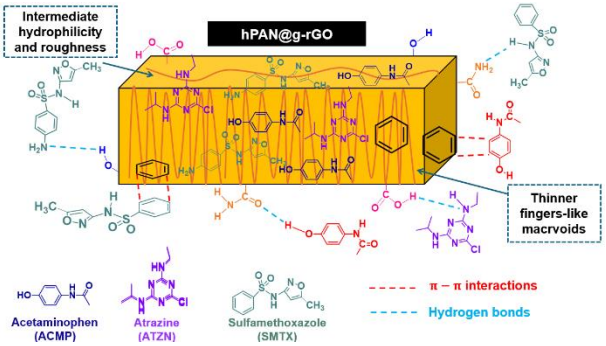

Fig. 5. Filtration mechanism.

4. Conclusions

The reduced graphene oxide was successfully produced by a green route with carrot extract. It was incorporated in a polyacrylonitrile membrane, causing an increase pure flux water, hydrophobicity, and roughness, and the formation of thinner finger-like sublayers. In adsorption experiments, the membrane hPAN@rGO-G3 enhanced antibiotics removal, and in filtration experiments the hPAN@rGO-G2 membrane showed the best removal for the ECs analyzed. The adsorption mechanism showed a removal hydrogen bonds, and $\pi - \pi$ and electrostatic interactions.

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