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Preparation of polymeric membranes containing green cationic rGO and their application in the removal of ciprofloxacin from water

Natália Gabriele Camparotto[a], Gabriel Henrique Silva Fulaneti[a], Melissa Gurgel Adeodato Vieira[b], Patrícia Prediger[a,*]

[a] *School of Technology, University of Campinas – UNICAMP, 13484-332, Limeira, São Paulo, Brazil.*
[b] *School of Chemical Engineering, University of Campinas – UNICAMP, 13083-852, Campinas, São Paulo, Brazil.*

Abstract

The presence of emerging contaminants in aquatic systems is a tangible phenomenon, due to their extensive and uninterrupted use, and the difficulty of removal in conventional sewage treatment systems. Consequently, the development of new and efficient technologies for eliminating these compounds is an urgent need. Among the various techniques available, adsorption is an advantageous approach. This work involved the preparation of reduced graphene oxide (rGO) functionalized with quaternary ammonium salt produced by the green route. Regarding the new cationic rGO material (rGO+), it is postulated that it will exhibit unique properties derived from positively charged rGO, which will confer a potential adsorbent capacity for electron-rich organic pollutants. rGO+ was incorporated into polymeric membranes and applied to adsorb ciprofloxacin from water. Adsorption experiments revealed that as the rGO+ content increased, the adsorption of ciprofloxacin increased, reaching 54 mg/g (68%). The new materials are considered promising adsorbents of antibiotics from water.

Keywords: adsorption; ciprofloxacin; polymeric membranes; reduced graphene oxide.

1. Introduction

The presence of antibiotics in water resources has caused significant environmental concern, as these compounds are not completely removed by conventional treatment methods. This class of compounds, when present in water, can be persistent and contribute to numerous adverse effects on human health and the environment [1].

Ciprofloxacin (Figure 1) is an antibiotic that targets gram-negative and gram-positive bacteria in human and veterinary medicine and is often used for serious bacterial infections. The presence of this antibiotic in the environment is a significant concern due to its potential toxicity to non-target organisms [2].

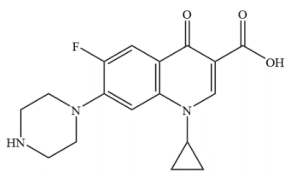

Figure 1. Chemical structure of ciprofloxacin.

Adsorption is a technology that has been widely employed due to its numerous benefits, including high efficiency, ease of handling, and low cost [3,4]. Graphene oxide (GO), derived from the oxidation of graphite, has emerged as an excellent adsorbent due to its high surface area and hydrophilicity. The removal of aromatic organic compounds by GO can be enhanced by reducing it to reduced graphene oxide (rGO), with the return of some double bonds. This process facilitates interactions with aromatic pollutants through $\pi-\pi$ interactions [5].

Several research groups have developed environmentally friendly synthetic pathways for the reduction of GO to rGO [6]. Moreover, rGO exhibits high efficiency in the adsorption of electron-poor organic pollutants. One strategy to reduce the negative surface charge of rGO is the insertion of positively charged groups.

A limitation of using rGO in water treatment is the difficulty of removing it from water after decontamination. An alternative approach to this issue is the immobilization of rGO on polymeric supports, such as membranes [7,8].

The objective of this study was to prepare reduced rGO from the green route using residual

carrot biomass extract as a reducing agent. Furthermore, we aimed to covalently insert a quaternary ammonium salt using ionic liquid as a solvent for esterification. Afterwards, we immobilized the synthesized material on polyacrylonitrile membranes. The synthesized green cationic rGO (rGO+) and the prepared membranes containing different contents of rGO+ were characterized using different techniques and applied to the removal of the antibiotic ciprofloxacin.

2. Methods

2.1. Green cationic rGO (g-rGO) synthesis

Firstly, the residual carrot biomass extract was employed as a reducing agent to reduce GO to rGO (Figure 2), in accordance with the methodology proposed by Silva et al. [9].

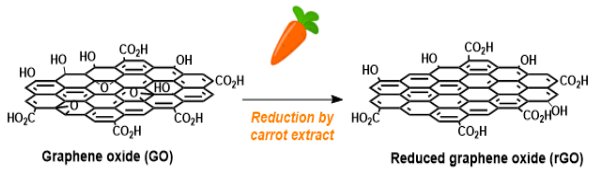

Figure 2. Reduction of graphite oxide (GO) to reduced graphene oxide (rGO) using residual carrot biomass extract as a reducing agent.

The subsequent stage of the process entailed the functionalization of the rGO produced by the green route with quaternary ammonium salt derived from the esterification reaction with N,N-dimethyl-2-hydroxyethylamine (Figure 3). This was achieved using the ionic liquid 1-methylimidazolium tetrafluoroborate ([MIM]$^{+}$BF4) as green solvent and catalyst, according to the esterification protocol proposed by Halligudi et al. [10].

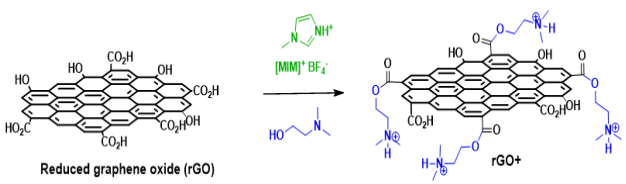

Figure 3. Representation of the preparation of rGO+ via the green route using ionic liquid as the green solvent.

2.2. g-rGO+@PAN synthesis

The initial step involved the preparation of a solution composed of 2 g of polyacrylonitrile (PAN) and 0.22 g of lithium chloride in 16 mL of dimethylformamide (DMF). The mixture was subjected to magnetic stirring at 60 °C until complete dissolution was achieved. Subsequently, the membranes were generated using the phase inversion method, as proposed by Neves et al. [8]. with different contents of rGO+. To this end, 10%, 20%, and 30% (% w/w) of rGO+ were added to the prepared PAN solution and subjected to magnetic stirring until a homogeneous solution was achieved. Subsequently, 0.5 mL of the prepared solutions were poured into Petri dishes and submerged in ultrapure water to form the membrane. The membranes were maintained in ultrapure water to prevent loss of texture due to moisture evaporation (Figure 4).

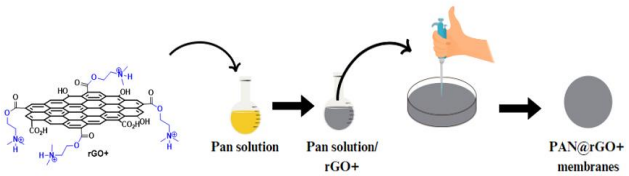

Figure 4. Preparation scheme for PAN@rGO+ membranes.

2.3. Characterization

Zeta potential: Measurements of zeta potentials (mV) of rGO and rGO+ were carried out for the pH range from 4 to 8 using the Zetasizer Nano ZS equipment (Malvern).

Fourier transform infrared (FTIR): Functional groups were analyzed by FTIR. The apparatus employed was an Agilent Cart 630 FTIR, using the KBr pellet method, with a scan extending from 4,000 to 400 cm^{-1}.

2.4. Adsorption experiments

Batch adsorption tests were conducted with a concentration of 50 mg/L of ciprofloxacin. The system was agitated for 24 hours, after which the collected samples were diluted and analyzed by UV-vis spectroscopy, based on the previously determined standard curve. All tests were conducted in triplicate.

3. Results and discussion

3.1. Characterization

The FTIR spectra of GO and rGO are shown in Figure 5. The GO spectrum exhibits bands at 3479, 2929, 2851, and 1740 cm^{-1}, which are attributed to the presence of hydroxyl, carbonyl, and ketone groups, respectively. The rGO spectrum showed a discernible decline in the intensity of the OH band. These findings provide corroborating evidence that graphene oxide was effectively reduced.

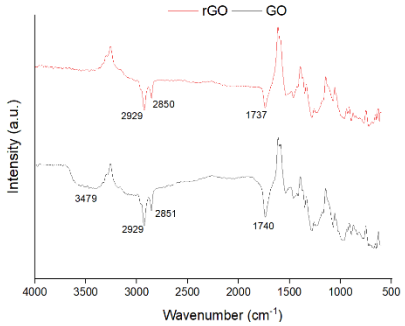

Figure 5. FTIR spectra of GO and rGO**.**

Zeta potential analysis was conducted to verify the surface charge of the material prepared (Figure 6). Pristine rGO exhibited zeta potential values ranging from −18 mV to −36 mV within the analyzed pH range (pH 4 to 10).

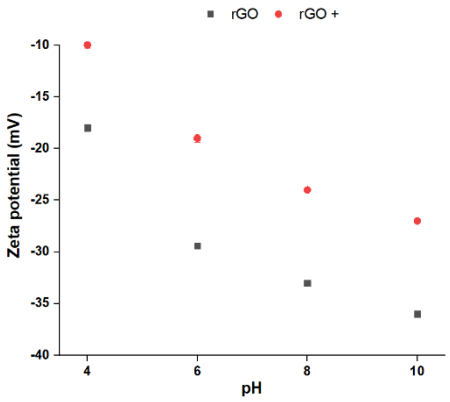

Figure 6. Zeta potential analysis of rGO and rGO+.

In contrast, rGO+ exhibited less electronegative values in the pH range analyzed, from −10 to −27 mV, thus confirming the functionalization of rGO with a quaternary ammonium salt.

3.2. Adsorption assays

Adsorption tests were carried out using membranes with pristine rGO (PAN@rGO) and rGO+ (PAN@rGO+ 10%, 20% and 30% w/w) (Figure 7). The results indicated that the membranes containing rGO+ exhibited greater adsorption potential than the PAN@rGO membrane (17 mg/g) for the removal of ciprofloxacin from water. The adsorption capacity exhibited a notable increase in removal capacity when rGO+ was added to the membrane. The removal capacities were 30, 47, and 54 mg/g, for PAN@rGO+ containing 10, 20, and 30% (w/w) rGO+, respectively. These results are promising, as the presence of rGO+ enhanced the adsorbent capacity to remove ciprofloxacin from water.

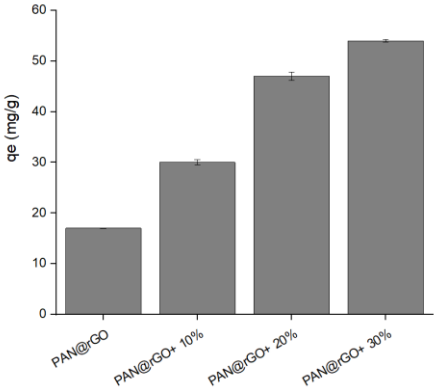

Figure 7. Removal of ciprofloxacin from water by PAN@rGO and PAN@rGO+ membranes (10%, 20% and 30% w/w).

The removal of the antibiotic by PAN@rGO+ indicates that the presence of rGO+ facilitates interactions such as π-π, electrostatic, and hydrophilic interactions, which play an important role in the adsorption process. Also, the findings demonstrate that a high proportion of rGO+ within the membrane enhances the adsorption characteristics of the adsorbent in contaminant removal.

Optimization of the adsorption system is currently underway. The methodology employed in this study represents a novel approach that facilitates the production of effictive and promising

adsorbent material for the removal of ciprofloxacin from water.

4. Conclusions

In this study, new promising adsorbents were developed for the removal of ciprofloxacin from aqueous solutions. rGO and rGO+ were synthesized and PAN@rGO+ membranes in different proportions (10%, 20%, and 30% w/w) were prepared. Adsorption tests demonstrated that the membrane comprising rGO+ exhibited superior ciprofloxacin removal efficiency compared to the pristine rGO membrane.

Acknowledgements

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References

[1] B.P. Rickard, I. Rizvi, S.E. Fenton, Per- and poly-fluoroalkyl substances (PFAS) and female reproductive outcomes: PFAS elimination, endocrine-mediated effects, and disease, Toxicology. 465 (2022) 153031. https://doi.org/10.1016/J.TOX.2021.153031.

[2] K.R. Kelly, B.W. Brooks, Global Aquatic Hazard Assessment of Ciprofloxacin: Exceedances of Antibiotic Resistance Development and Ecotoxicological Thresholds, in: 2018: pp. 59–77. https://doi.org/10.1016/bs.pmbts.2018.07.004.

[3] E.S. Avila, C.C.N. Melo, T.P. Sampaio, F.M. Machado, Síntese e caracterização de óxido de grafeno e óxido de grafeno reduzido, Rev. Bras. Eng. e Sustentabilidade. 3 (2016) 19–24.

[4] T.S. Anirudhan, J.R. Deepa, Nano-zinc oxide incorporated graphene oxide/nanocellulose composite for the adsorption and photo catalytic degradation of ciprofloxacin hydrochloride from aqueous solutions, J. Colloid Interface Sci. 490 (2017) 343–356. https://doi.org/10.1016/j.jcis.2016.11.042.

[5] P. Prediger, T. Cheminski, T. de Figueiredo Neves, W.B. Nunes, L. Sabino, C.S.F. Picone, R.L. Oliveira, C.R.D. Correia, Graphene oxide nanomaterials for the removal of non-ionic surfactant from water, J. Environ. Chem. Eng. 6 (2018). https://doi.org/10.1016/j.jece.2018.01.072.

[6] B. Li, X. Jin, J. Lin, Z. Chen, Green reduction of graphene oxide by sugarcane bagasse extract and its application for the removal of cadmium in aqueous solution, J. Clean. Prod. 189 (2018) 128–134. https://doi.org/10.1016/j.jclepro.2018.04.018.

[7] M. Khansanami, A. Esfandiar, High flux and complete dyes removal from water by reduced graphene oxide laminate on Poly Vinylidene Fluoride/graphene oxide membranes, Environ. Res. 201 (2021) 111576. https://doi.org/10.1016/J.ENVRES.2021.111576

[8] T. de F. Neves, N.G. Camparotto, E.A. Rodrigues, V.R. Mastelaro, R.F. Dantas, P. Prediger, New graphene oxide-safranin modified@polyacrylonitrile membranes for removal of emerging contaminants: The role of chemical and morphological features, Chem. Eng. J. 446 (2022) 137176. https://doi.org/10.1016/J.CEJ.2022.137176.

[9] P.M.M. da Silva, J.A. Malvestiti, N.G. Camparotto, J.C. Pinto, V.R. Mastelaro, R.F. Dantas, P. Prediger, Novel Polymeric Membranes Based on Green Reduced Graphene Oxide for the Nanofiltration of Emerging Contaminants from Water in a Ternary System, Sep. Purif. Technol. Submitted (2024).

[10] T. Joseph, S. Sahoo, S.B. Halligudi, Brönsted acidic ionic liquids: A green, efficient and reusable catalyst system and reaction medium for Fischer esterification, J. Mol. Catal. A Chem. 234 (2005) 107–110. https://doi.org/10.1016/j.molcata.2005.03.005.