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Sustainability Spotlight Statement

Access to safe water is one the most basic human need for health and well-being. Considering the fast population growth as well as the increase water needs from agriculture, industry, and energy sectors, it is crucial to discover sustainable processes for water purification. The development of new technologies using nanoporous materials seems to be efficient to remove pharmaceutical micropollutants from water streams.

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Ionic and Non-ionic Organic Porous Adsorbents for the Removal of Chloramphenicol and Ciprofloxacin from Water

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Nanoporous organic materials with varying pore sizes were utilized to remove antibiotics from surface and groundwater. These adsorbents belong to the group of Covalent Organic Frameworks (COFs), known for their high stability, porosity, and large surface area. Given their characteristics, which are well-suited for adsorption applications, these materials demonstrated relatively high capture capacities for emerging organic pollutants such as chloramphenicol (182 mg/g for RIO-55) and ciprofloxacin (79 mg/g for RIO-55) compared to other organic porous adsorbents. To conduct a comparative study on adsorption efficiency, both ionic and non-ionic materials were selected. Some ionic materials exhibited greater affinity for pharmaceutical compounds due to different adsorption mechanisms. Additionally, tests using a real water sample from the Tagus River confirmed the materials' removal efficiency. A correlation was observed between the maximum adsorption capacity and the pore width of the COFs, suggesting that better fitting of these adsorbates into mesopores enhances adsorption performance.

[†] Footnotes relating to the title and/or authors should appear here.

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Introduction

The treatment of wastewater from industries or domestic consumption has been increasingly studied to improve the techniques and methodologies used, achieving greater efficiency¹. The growing number of organic pollutants found in water samples from rivers, lakes, and oceans, among others, is worrying, since persistent pollutants have been increasing over time, already known by industries, environmental networks, and researchers. Additionally, there are now new risks associated with the so-called emerging pollutants², including active pharmaceutical ingredients (API). About 50% to 90% of an API dosage is eliminated unchanged to nature and these compounds persist in the environment^{3,4}.

Of the persistent drugs, antibiotics are a class of greatest concern among environmentalists⁵. This is the largest category of drugs provided by human and veterinary medicine, with therapeutic purposes or as growth promoters. The increase in the consumption of antibiotics consequently generates greater disposal in the environment. Because of its use in fish culture, some antibiotics such as chloramphenicol are found in sediments of marine origin⁶. Several antibiotics can be found in wastewater due to inadequate disposal of unused drugs or their incomplete metabolism in humans⁷.

The removal efficiency of these organic pollutants in water and sewage treatment plants is minimal. This is because conventional treatment technologies have limitations in removing a variety of APIs^{8–10}. Thus, new approaches involving liquid-liquid extractions, adsorption, and membrane technology have been reported to remove these and other pollutants from water. In recent years, conventional porous materials such as activated carbons and bioceramics have been mainly tested as adsorbents for water treatment processes^{11,12}. However, they cannot capture many of the organic pollutants and heavy metals that may exist in the water to be treated^{13,14}. An emerging class of organic nanoporous materials called Covalent Organic Frameworks (COFs) have shown to be good candidates for capturing gases, ions, molecules, and biomolecules^{15–21}. Hence, this class of porous materials has been selected as organic adsorbents, as they are thermally stable, and possess high porosity as well as high specific area values. These materials are formed by light elements owning different classifications according to their structure and physicochemical properties. In general, COFs can be two- or three-dimensional, ionic, or non-ionic and their synthesis can be adjusted according to the purpose of the material, forming a highly insoluble powder. They have been used for a variety of applications, especially for energy fields and environmental problems^{22–24}.

Herein, selected nanoporous organic materials previously prepared by our group^{25–27} called RIOs (acronym for Reticular Innovative Organic materials, Figure 2), which can be non-ionic

(RIO-12, RIO-13, RIO-24), and ionic (RIO-55 and RIO-70) are evaluated as adsorbents of ciprofloxacin and chloramphenicol antibiotics from water. The micro- and mesoporous structures of RIOs are selected to assess the effect of pore size and nature in adsorption processes.



Figure 1. The structure of a non-ionic and an ionic COF (top), the definition of porosity (middle), and the chemical structures of the chloramphenicol (CLO) and ciprofloxacin (CIP).

Experimental

Synthesis and Characterization of RIOs

RIO-12, RIO-13, RIO-55, and RIO-70 were synthesized as reported in previous studies ^{28–30}. On the other hand, RIO-24, to our knowledge, was never previously reported. RIO-24 was synthesized by solvothermal synthesis, where melamine (110 mg, 0.87 mmol) was added to triformylphloroglucinol (250 mg, 1.2 mmol). The solid mixture was transferred to a 48 mL high-pressure vessel (ChemGlass) and then DMSO (15 mL) and then HOAc 3M (3 mL) were sequentially added. The reactor was closed and remained under stirring and heating (190 °C) for 3 days, resulting in a dark red powder. All detailed synthesis and physicochemical characterization of RIO-24 are included in the Supplementary information (ESI).

The adsorbents were characterized as previously reported. The analysis of textural properties (isotherms and pore size distribution) is placed on ESI. RIO-24 was characterized by FTIR, CP-MAS ^{13}C NMR, PXRD, N₂ adsorption and desorption.

Thermodynamic studies of adsorption

To study the adsorption of organic pollutants in water, the nanostructured porous materials were used as adsorbents, and the antibiotics chloramphenicol (CLO) and ciprofloxacin (CIP) as adsorbates (Figure 1). Aiming to relate the structure properties of these materials with their adsorption capacity, ionic and non-ionic

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adsorbents, micro and mesoporous, have been selected. Figure 2 illustrates the comparative structure of the selected ionic dyebased (RIO-55 and RIO-70), melamine-based (RIO-24), and hydrazine-based (RIO-12 and RIO-13) materials.

Solutions of chloramphenicol and ciprofloxacin from commercial sources (Alfa Aesar <98% and TCI <98%, respectively) were prepared in different concentrations (5-80 ppm and 4-22 ppm, respectively). Each solution was previously analysed by UV-vis (200-500 nm) to obtain the absorbance data, where λ_{max} (chloramphenicol)= 272 nm and λ_{max} (ciprofloxacin)= 278 nm. The absorbance data were plotted versus concentrations, obtaining a straight line (calibration curve), whose equation allows for correction of the final values of concentration and absorbance (Figure S13). Then, 4mg of adsorbent was added to 4mL of each sample, which was placed in a shaker (2400 rpm) for 4h and 24h to observe the different values of adsorption. After this, the samples were filtered in specific filter papers (Glass microfibre, 55 mm, Filter Lab for CIP; Qualitative filter paper, 1300/80, 70 mm, Filter Lab for CLO) for each drug, previously tested to check any influence of paper in absorbance. After the filtration, the adsorbent remained on the filter paper, while the resulting solution was taken for UV-vis analysis (200-500 nm), obtaining the final values of absorbance. The method chosen to quantify the adsorption capacity was made by the difference in concentration (initial vs final).

Effect of pH on the adsorption

The capture of these antibiotics in a wide pH range is highly desirable for practical waste disposal. Thus, isothermal adsorption curves in different pH values (1.5 - 12.5) for RIO-70 and RIO-24 were determined. These RIOs were chosen to compare the pore size and adsorption capacity. In general, 4mg of adsorbent was added to a solution of 4 mL containing the micropollutant (50 ppm for CLO and 10 ppm for CIP). The pH adjustments were performed using a correspondent solution of HCl or NaOH (0.1M). The samples were left in a shaker for 10 min and then filtered and analysed by UV-vis. Then, the pH of the solutions was measured.

Regeneration cycles

Aiming to obtain information about the reuse of these materials after the first adsorption (RIO-70 and RIO-24), regeneration tests have been performed. For these studies, 10 mg of adsorbent was added to 10 mL of pollutant solutions. For chloramphenicol, the 50 ppm solution was used while for ciprofloxacin only 10 ppm was selected. The samples were left in a shaker for 30 min and then filtered and analysed by UV-vis. The adsorbent was retained on filter paper and then reused. For the desorption process, the materials were immersed in 70 mL of methanol under stirring (shaker) for 6 min. After this, the solution was filtered again and the solid remained in contact with new pollutant solutions. This process was carried out consecutively for 4 times in the case of CLO and 3 times in the case of CIP.

Pollutant removal from a real water sample

Pollutant adsorption tests were performed from a real water sample, taken from the Tagus River in Portugal. Firstly, the real sample was analysed by UV-vis to observe the adsorption bands present in the selected wavelength range (200-500 nm). When confirming the absence of absorption bands at 272 nm and 278 nm respectively (CIP and CLO), the solutions with the same concentrations as the tests described above were prepared. The calibration curves of the river water samples containing the same micropollutants were made by UV-vis spectroscopy as shown in Figure S15 (ESI). A good correlation was obtained for both cases $(R^2 > 0.99)$. Thus, the antibiotics were included in the real sample. For the real assays, 4 mg of each adsorbent (RIO-70 and RIO-24) was left in contact with 4 mL of pollutant solutions in a shaker for 24h at 2400 rpm. After that, the solutions were filtered and analysed, as done in the previous conditions considering the same selected wavelength range (200-500 nm).

Results and Discussion

The nanoporous adsorbents, RIOs, were selected according to their porosities and chemical structures including non-ionic (RIO-12, RIO-13, and RIO-24) and ionic (RIO-55 and RIO-70) organic materials (Figure 2). ¹³C NMR for RIO-24 exhibited an intense signal at ~166 ppm indicative of the triazine carbon. At ~184 ppm a C=O signal appears, showing the structure's preference for the keto-enamine form. However, a signal at ~54 ppm indicates that the structure is also formed for aminal-type bonds (N-CH-N). Probably, these connections must be pillaring the structure, which forms larger spaces, being detected as mesoporous (see Figure S07). N₂ adsorption/desorption isotherm showed a hysteresis, typical of mesoporous materials, classified as type IV. The surface area obtained by the Brunauer-Emmett-Teller (BET) equation was 650 m²/g, of which 248 m²/g refers to a microporous area and 402 m²/g to a mesoporous area, according to the calculated t-Plot (De Boer). Pore size distribution indicated pores of 14 and 50 Å (see Figure S07 inset). The PXRD for RIO-24 presented low crystallinity possessing an intense peak at $\theta \sim 29^\circ$ in agreement with forming a lamellar structure.

From the absorbance data obtained (see ESI, Figure S14), it was possible to find the final concentration values (Ce), according to the number of pollutants that have not been adsorbed by the RIOs. Therefore, the difference method (Ci-Ce) was applied to obtain the maximum adsorbed amount or adsorption capacity (Q_{max}). A Langmuir isotherm was generated for each of the adsorption processes, by plotting Q_e versus C_e . From its non-

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adsorbent at equilibrium (mg/g), and K_L is the constant interaction

between the adsorbate and the adsorbent.

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linearized form, the Q_{max} and K_L parameters were obtained, plotting C_e/Q_e versus C_e , according to the following equation:

$$\frac{\text{Ce}}{\text{Qe}} = \frac{1}{\text{Q}_{\text{max}}} \text{Ce} + \frac{1}{\text{K}_{\text{L}}.\text{Q}_{\text{max}}}$$

where Ce (mg/L) is the final concentration or concentration at equilibrium, Qe (mg/g) is the amount of pollutant adsorbed at equilibrium, Q_{max} is the maximum adsorption capacity of



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Ionic materials NH₂CI OF OH СНО оно ·2HCl он HO H₂N ćно сно **Bismarck Brown Y** TFPG Pararosaniline TFPG hydrochloride 1,4-dioxane 1.4-dioxane 120°C/72h 120°C/72h **RIO-55 RIO-70**

Figure 2. The non-ionic and Ionic nanoporous organic materials are used as adsorbents in this work.

From the CLO and CIP calibration curve, the Ce values were adjusted according to the following equation:

 $C_e = (Abs_{initial} - b)/a$

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where the parameters *a* and *b* are obtained through the equation by plotting concentration versus absorbance, according to the Lambert-Beer law. The calibration curves obtained for CLO and CIP are in Figure S13 (ESI).

However, some isotherms were also plotted following Freundlich's theory. The equations and parameters suggested by this model are related to the heterogeneity of the adsorbents and the multilayers that can be formed into the pores and the surface. Then, the linearized form of Freundlich equations is:

 $\log Q_e = \log K_F + \frac{1}{n} \log C_e$

where K_F is the Freundlich constant, representing the interception, and 1/n is the parameter correlated to the adsorption intensity, the slope, whose values can be attributed to stronger or weaker interactions between the adsorbates and adsorbent. If n>1, this attraction is more relevant, presenting a great affinity and suggesting more favourable adsorption, while 1/n=n=1 indicates that both adsorption sites have the same energy (linear form).

Figure 3 shows the Langmuir adsorption isotherms of CIP. The curves are classified as favourable, showing that the interaction between the adsorbent and adsorbate occurs as the concentration value increases, until equilibrium. The isotherms for RIO-70, RIO-24, and RIO-13 are considered L-type (Langmuir), the most common for carbonaceous surfaces. On the other hand, RIO-55 has an F-type isotherm, indicating some superficial heterogeneity. This classification is based on adsorption processes on solids, where it is possible to see different surfaces in the same material and their levels of interaction with adsorbates.

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Figure 3. Ciprofloxacin (CIP) adsorption isotherms (Langmuir model) and its non-linearized form (inset).

The ionic and mesoporous RIO-55 removed more CIP at room temperature. The values show that RIOs with larger pores such as RIO-55 and RIO-24 captured a greater amount of CIP due to the diffusion in the pores and on the surface. These diffusion steps occur in different ways, considering the size of the adsorbed molecules. It is important to note that this is a determining factor for microporous materials. In larger pores, molecules diffuse as if there were no pore walls. **Table 1** shows the values of Q_{max} and K_L obtained from the Langmuir equation non-linearized for pollutant removal, as well as the surface area (BET) as well as pore size of the adsorbents. **Figure 4** exhibits the Langmuir isotherms obtained for the adsorption of chloramphenicol (CLO) and its non-linearized form. As found for CIP, the CLO adsorption isotherms are of the favorable type, fitting with the Langmuir model, as the S (sigmoidal) type. However, the RIO-70 isotherm shows a more favorable curve, with a less pronounced convex slope.

About Freundlich's model, the linearized isotherms were carried out to determine the parameters and then be compared between the Langmuir ones. A summarized table was created to inform the obtained values for R^2 , 1/n for both models using all the RIOs and the antibiotics (see ESI). All the isotherms were of the favorable type (short values for 1/n and n>1) following the assumptions of Freundlich's theory. These data coincide with the parameters found for the Langmuir model, presenting favorable adsorption. In this way, the preference or affinity of adsorbents with antibiotics, especially CLO, is observed.

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Figure 4. Chloramphenicol (CLO) adsorption isotherms (Langmuir model) and its non-linearized form (inset).

Different adsorption mechanisms can occur during the process, such as the pore-size effect, π - π interaction, H-bonding, and hydrophobic interaction. As seen above, the pore size of RIOs is one of the determining factors for the capture of antibiotics. This is observed in situations where water is the fluid. There is also the contribution of hydrogen bonds, indicating greater adsorption of CLO than CIP, if we look at their structure. In addition, in the case of ionic materials, there are hydrophobic interactions due to the presence of charges. Therefore, RIO-55 is more effective because of a set of factors that allow it to absorb more antibiotics.

For the ionic RIOs, the electrostatic interactions are more dominant, as commonly shown in the published works. However, the supporting interactions perform an important job in the assembly. It is important to highlight that ciprofloxacin can exhibit different conformations, being easily ionized. This fact can contribute to more interactions between the RIOs and the antibiotic.

Besides that, the parameters applied from the Freundlich and Langmuir model show stronger interactions between the adsorbates and some COFs, mainly the ionic ones. Following Freundlich parameters, the values of n>2 show the adsorption intensity is greater in the ionic COFs than in the neutral. This suggests a strong intermolecular attraction between the solid and the adsorbates.

Some works reported different materials as adsorbents for other organic pollutants, such as β -cyclodextrin COF³¹ that captures 88 mg/g of bisphenol-A. Some commercial materials such as Brita AC and DARCO were used, capturing 19-24 mg/g of bisphenol-A. The porous material PDC-P captured 21 mg/g of bisphenol-S, 26 mg/g of propanol, and 22 mg/g of ethinyl estradiol. The COF-NO₂ captured 70 mg/g of Ketoprofen, 94 mg/g of Ibuprofen, and 84 mg/g of Naproxen³².

Adsorption tests with different pHs were performed for ciprofloxacin and chloramphenicol solutions, using RIO-70 and RIO-24 as adsorbents. **Figure 5a** shows the adsorption behaviour and the Q_e values obtained for each pH. The pH of the chloramphenicol solution used in the RIO-70 adsorption curves (i.e., no acid or base added) was 8.13; and by RIO-24, the pH was 7.45. Observing the behaviour of the points in the figure, it is noticed that, in these pH values, there was the smallest adsorbed

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amount (Q_e), for both adsorbents. RIO-70 adsorbed more of the CIP at a more basic pH (9.2), while RIO-24 adsorbed better at an acidic pH (3.5).

Table 1. Parameters from Langmuir equation considering CLO andCIP removal and textural properties of the COFs.

Ads	S _{BET} (m²/g)	Q _{max} (mg/g) CIP	K∟ CIP	Q _{max} (mg/g) CLO	K _L CLO
RIO-12	830	8.0	1.420	23.0	0.145
RIO-13	900	19.5	0.265	13.5	0.228
RIO-24	650	34.0	0.125	45.0	0.435
RIO-55	350	79.0	0.169	182.0	0.036
RIO-70	990	28.0	0.401	133.0	0.049

The pH of the ciprofloxacin solution used in the adsorption tests with RIO-70 was 8.59 while in the case of RIO-24 was 9.47. The adsorption values were not very discrepant with the pH change for

ciprofloxacin, for both materials. The Qe value is slightly better at more acidic pHs. It is also noted that the adsorption of chloramphenicol occurs faster when compared to ciprofloxacin. In about 30 min of contact (solution + adsorbent), the Qe value for both RIOs is higher for chloramphenicol.

The pollutant removal efficiency tests were performed after several cycles. After the first adsorption of chloramphenicol on the adsorbents, another four cycles of adsorption were employed, using the same material filtered and treated with methanol. RIO-70 lost more mass than the RIO-24 during the recycling process, due to the filtration step. Thus, only 4 to 5 cycles were performed for each material. Figure 5b shows the number of cycles and the percentage of chloramphenicol and ciprofloxacin adsorbed in each cycle. After 30 min of contact with CLO solution, the RIO-70 adsorbed about 70-80% of the pollutant, in an interval of 4 consecutive cycles. RIO-24 captured about 60% of CLO during the 4 cycles. In the last cycle, there was a slight drop in the adsorption value by the RIO-70, which may be due to the loss of mass during the filtration steps, which almost did not occur for the RIO-24. For CIP, there are only 3 cycles in total, due to the type of paper used to filter the solutions (microfiber), which retained the material. Despite this, both adsorbents captured good amounts of the pollutant, maintaining the adsorption capacity in the 3 cycles.

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Figure 5. (a) Adsorbed amount of CIP and CLO by RIO-70 and RIO-24 at different pHs; (b) Regeneration cycles of RIO-70 and RIO-24 for CIP and CLO.

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In addition to performing adsorption tests using milli-Q water, the efficiency of adsorbents in a real water sample was also tested. **Figure 6a** shows the CLO and CIP adsorption isotherms of RIO-70 and RIO-24. The Langmuir model was used, as well as its non-linearized form, from which the quantitative parameters (Q_{max} and K_L) were extracted. The obtained values of Q_{max} (CLO) for the real

sample and milli-Q water were very similar (133 mg/g for RIO-70 and 25 mg/g for RIO-24). The CLO adsorption curve for RIO-70 is L-type, proving to be highly favourable. Conversely, the RIO-24 curve is S-type, but less favourable since it leans after remaining constant.



Figure 6. (a) Adsorbed amount of CLO and (b) CIP by RIO-70 and RIO-24 in real water samples and their respective Langmuir non-linearized forms (inset).

The CIP isotherms adsorptions for RIO-70 and RIO-24 (Langmuir model) are S type, with a higher inclination for the RIO-24 curve, whose convex region is more pronounced (Figure 6b). The obtained Q_{max} values for both adsorbents in the real sample were practically the same compared to milli-Q water (28 mg/g for RIO-70 and 32 mg/g for RIO-24).

The similarity between the Q_{max} values found in the model tests and real water for the same pharmaceutical micropollutants shows the efficiency of removal by the adsorbents, in addition to proving to be selective for these compounds. The UV-vis spectra of the real sample exhibited an absorbance at ~200 nm, which decreased considerably after contact with the adsorbents. At ~350 nm, it was also possible to notice a less pronounced absorption band, which disappeared after adsorption (See Supporting Info for more details).

Molecular interpretation

The data expressed in mass proportion (*i.e.*, mg/g) can be useful for engineering or practical reasons. However, for a better

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comprehension of the possible phenomenon, one should look at the number in (mol of API)/(mol of pores) to determine how many molecules of a given API can be included in the pore system. This enables the comparison of the performance of various COFs with different molecular masses per unit cell. **Figure 7** demonstrates, for instance, that the unit cell of RIO-55 (blue), which has the $C_{72}N_{24}H_{54}O_6$ and a molar mass (MW) of 1351.3866 g/mol, contains a single pore (yellow). That is valid for any COF with the same topology as RIO-55.



Figure 7. Demonstration of the unit cell of RIO-55 forming a single pore.

Thus, the molecular ratio of a given API per pore can be calculated as

Loading per pore =
$$\frac{Q_{max}(mg)/MW(API)}{1g/MW(unit cell)}$$

Table 2. Molar ratio between the amount of API per pore for the COFs used in this study.

COF	Pore width	Unit cell of the COF		API per pore (mol/mol)	
	(Å)	Formula	MW* (mol/g)	CIP	CLO
RIO-12	11	$C_{18}N_6H_{12}O_4$	376.3333	0.01	0.03
RIO-13	11	$C_{18}N_6H_{12}O_6$	408.3321	0.02	0.02
RIO-24	8.8	$C_{12}N_6H_6O_3$	282.2196	0.03	0.04
RIO-55	34	$C_{72}N_{24}H_{54}O_6$	1351.3866	0.32	0.76
RIO-70	10	$C_{28}N_{3}H_{18}O_{3}CI$	490.0047	0.05	0.20

*MW=molar mass of the unit cell

Table 2 shows the molar ratio of the APIs per pore for CLO and CIP and the pore size of the COF. It is noteworthy that RIO-55 is the only COF that holds considerable amounts of API molecules into the pore system. This is related to its pore width since RIO-55 has the largest pore system among the COFs studied. Actually one can observe a correlation between pore width of the COF and its ability of capture of the API (Figure 8).



Figure 8. Correlation of the loading of the API per pore (molar ratio) as a function of the pore width of the COF.

Analysis of the geometries of the APIs and the pore systems of these COFs shows that only RIO-55 can comfortably fit the APIs into its pore system, indicating that the other COFs may have diffusion problems for adsorbing them (Figure 9).



Figure 9. Experimental geometries (x-rays) of the APIs and pore dimensions of RIO-12 (lower left) and RIO-55 (lower right), calculated from the quantum chemical level optimized structure at DFT level.

Thus, it is plausible that mesoporous COFs are more suitable for the adsorption of APIs compared to microporous COFs. This can be a guideline for the design of new nanoporous materials for such a goal.

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Conclusions

Ionic and non-ionic nanomaterials were pre-selected from their structural design and porosity to capture organic pollutants from water. For this, the antibiotics ciprofloxacin and chloramphenicol were chosen as adsorbates since they have increased their occurrence in the water of rivers and seas. Generally, it was observed that materials with larger pores adsorb more pollutants. The removal efficiency is higher for materials composed of ionic structures, such as RIO-55 and RIO-70. The strong interactions between the adsorbates and RIOs were determined by Langmuir and Freundlich parameters from linearized equations. These ionic materials can show more different ways of interaction, mainly electrostatic and hydrogen bonds. The Qmax values obtained for RIOs are higher in the literature for other organic pollutants. In addition, pH studies were performed, where the pollutants removal at different pHs varied considerably. RIOs can be regenerated at least 3 to 5 times, showing a good adsorption capacity, even after successive cycles of reuse. Finally, samples of real water from the Tagus River collected in Portugal were used to obtain the adsorption capacity of antibiotics by the selected materials, even competing with other molecules or existing fluids. The Q_{max} values obtained were similar or equal to the samples with pure water. RIOs presented better adsorption capacities than several adsorbents already reported. Indeed, this shows the good selectivity of these materials to CLO and CIP antibiotics and their removal efficiency. A correlation between molar ratio of the maximum quantities of the APIs and the pore width of the COFs was observed. This shows that only RIO-55 has enough space into the pore system to accommodate the APIs.

Author Contributions

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript. Sunny K. S. Freitas, Leticia R. C. Correa, and Verônica D. da Silva carried out the experiments and analysed the results. Luis C. Branco and Pierre M. Esteves formulated the concept of the project, planned the experiments, and managed the project.

Conflicts of interest

There are no conflicts to declare.

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Data Availability Statement

The data supporting this article have been included as part of the Supplementary Information.