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Study of the efficiency of the removal of steroid hormones from water by reverse osmosis

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Abstract: Water contamination by micropollutants is increasing, including steroid hormones. Indiscriminate use, incorrect disposal, inefficient treatment of water and effluents, and less restrictive legislation promote the contamination of effluents and water, with harmful consequences for the environment and human health. In this work, it was evaluated the use of reverse osmosis in the removal of ethinylestradiol and levonorgestrel, synthetic steroids that are components of contraceptives. The hydraulic permeability of the membrane was assessed before, during, and after reverse osmosis of an aqueous solution of contraceptive, as well as the retention of hormones, of a synthetic solution of contraceptive used as the feed. 95.6% retention of the compounds was observed, demonstrating the efficiency of reverse osmosis in the removal of solutes. In addition, there was no important reduction of the hydraulic permeability of the membrane was efficient in removing fouling or other interferents formed during the process. Reverse osmosis was efficient in the removal of constituents of contraceptives from aqueous solutions, being an option in the treatment of water and effluents aiming to attain better potability and smaller toxicity risks for the environment and human health.

Keywords: Membrane separation processes, treatment of effluents, contraceptives, hydraulic permeability.

Introduction

With the increase of industrialization and the development of new technologies, there was the development of new products that contain chemical substances with the potential to harm human and animal health, even in concentrations in the range of micrograms per liter ($\mu g \cdot L^{-1}$) and nanograms per liter ($ng \cdot L^{-1}$). Steroid hormones fall under these micropollutants, being produced both naturally and synthetically. Their use in the pharmaceutical area includes uses in drugs, anabolic agents, and for stimulating the growth of animals, mainly for meat production [1].

Steroid hormones are examples of endocrine disruptors and may be natural, such as 17- β -estradiol and estrone, or synthetic, such as 17- α -ethinylestradiol [1]. Endocrine disruptors are considered micropollutants because they have biological effects in the range of parts per billion (ppb – $\mu g \cdot L^{-1}$) or parts per trillion (ppt – $ng \cdot L^{-1}$) in water and effluents. These

hormones are excreted by the human body in low concentrations, and due to failures and limitations of water and effluent treatment systems, they end up in water bodies and return to the water for human consumption. Because of this, they can pose a health hazard, altering body functions and metabolism. In addition, they affect aquatic ecosystems, causing hormonal dysfunction and gender change in aquatic animals, in addition to the potential for bioaccumulation [2].

According to Halluch [3], steroids can cause aesthetic problems, such as acne and hair loss, to health problems related to the cardiovascular, nervous, and hepatic systems. There is also the possibility of alterations in blood pressure, in addition to increasing the chances of developing thrombosis and atherosclerosis. In addition, sexual dysfunctions are related to excess steroids. Among them, there is virilization and masculinization in women, such as a deepening of the voice and an increase in the amount of hair, as well as the feminization of men, resulting in impotence and male sterility, as well as a decrease in the production and quality of semen. Other relevant effects are those referring to the central nervous system, among them the development of mood problems, irritability, aggression, insomnia, and even depression.

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According to Nicolopoulou-Stamati and Pitsos [4], endocrine disruptors can affect the female reproductive system since it depends on a balance between hormones. There is evidence that relates endocrine disruptors to abnormalities of the menstrual cycle, ovulation, woman fertility, and pregnancy. Additionally, endocrine disruptors may have effects on conditions such as endometriosis, polycystic ovary syndrome, and tumors in the male and female reproductive system.

Studies show that several Brazilian water resources contain micropollutants. Even after water and effluent treatment, these compounds are still present in water intended for human consumption. Hormones such as ethinylestradiol, estriol, estrone, levonorgestrel, and 17- β -estradiol were found in watersheds of the states of Minas Gerais, São Paulo, and Rio de Janeiro, their presence being confirmed in samples of raw and treated water. Concentrations in the range of 5 – 30 ng·L⁻¹ were observed, except for levonorgestrel, which was found in concentrations above 300 ng·L⁻¹, being this steroid is one of the main components of several contraceptives widely used [5-6].

The contamination of hydric resources with steroid hormones can also occur due to animal husbandry, which is often treated with steroids to accelerate growth and development. Five water sources in the US state of Arkansas were analyzed for the presence and content of 17- β -estradiol, these sites being surrounded by livestock and poultry crops (chickens and turkeys). The transfer of hormones from the animals to the ground and water occurs through feces and urine, carrying contaminants for kilometers through canals, streams, and groundwater. The presence of estradiol was verified in all foci, with concentrations varying in the range of 6-66 ng·L⁻¹ [7].

According to Teixeira et al. [8], steroid hormones were found in effluents from the University of São Paulo. Both in the raw sewage and the treated effluent, the concentrations of these endocrine disruptors were high, reaching 7.34 μ g·L⁻¹ for 17- β -estradiol in the raw sewage and 7.74 μ g·L⁻¹ in the treated effluent. For estrone, estradiol, and ethinylestradiol, the detection frequency was 100%, i.e., in all collected samples these hormones were present. For estriol, the detection frequency was 75%.

In samples of raw sewage from ETE São João, in Porto Alegre, the hormones estrone, estradiol, and ethinylestradiol were detected with a frequency of 100%, with maximum concentrations of 8.85 ng·L⁻¹ of estrone and 6.57 ng·L⁻¹ of 17- β -estradiol. For ethinylestradiol, the concentrations were below the quantification limits. These waters, after treatment with activated sludge, were used for corn irrigation. As these hormones can cause adverse effects from 1.0 ng·L⁻¹, the concentrations found cannot be neglected [9].

According to Hartmann et al. [10], steroid hormones were detected in foods marketed in Germany. The hormones investigated were progesterone, testosterone, 17- β -estradiol, and estrone, in addition to their precursors, such as 17- α -ethinylestradiol and estriol. A likely origin of the hormones was the treatments given to animals containing these growth-accelerating steroids, making their meat, milk, and eggs subject to high concentrations of these hormones. The

vegetables, on the other hand, may have been contaminated through irrigation containing these micropollutants.

Even with no legislation that regulates the disposal of steroidal hormones in water bodies and their presence in drinking water for human consumption, several studies have been and are being carried out aiming to remove micropollutants from water. Methods including ultrafiltration, nanofiltration, reverse osmosis, filtration with granulated activated charcoal, oxidative processes, ozonation, and catalytic photoreduction are being explored for the decontamination of water and effluents [11].

According to Santos [12], conventional water treatment processes can be implemented associated with other water decontamination techniques for water and effluents containing hormones and other micropollutants. According to the same author, only the conventional treatment was not able to remove the micropollutant estradiol efficiently, and the raw showed practically the and treated samples same concentration of the steroid. The methods using the standard treatment and subsequent filtration with granular activated charcoal and the standard treatment preceded by oxidation with sodium hypochlorite showed better performance for hormone removal, with efficiency in the range of 86–90%.

Among the advanced effluent treatment processes, membrane separation processes have the advantage over conventional processes due to lower energy consumption since the temperature is not a main factor in separation; selectivity, making it possible to obtain purer species with more separation efficiency; the separation of thermolabile compounds, as they are normally operated at room temperature; and the simplicity of operation and the possibility of scaling, since the systems are modular [13].

The most widespread processes that use membranes are microfiltration, ultrafiltration, nanofiltration, reverse osmosis, dialysis, electrodialysis, gas permeation, and pervaporation. The kind of process and membrane are selected in agreement with the species to be separated, being fundamental in knowing molecule/particle size and the mechanism that characterizes each process [13].

Reverse osmosis is used for processes where it is desired to separate a solvent from low molecular weight solutes, such as inorganic salts. In this process, dense membranes are used, and the transmembrane pressure applied is higher, in the range of 20–100 bar. It is also important that the reverse osmosis membrane has a higher chemical affinity with the solvent and a lower affinity with the solute so that the system has greater separation efficiency [13-14].

Nghiem et al. [15] evaluated four reverse osmosis membranes in removing estradiol and estrone from water. The authors observed that estrone retention was above 98% for both hormones, in the four membranes. Silva et al. [16] studied the process of reverse osmosis for the removal of the hormones 17- β -estradiol, 17- α -ethinylestradiol, and estriol present in effluents of a sewage treatment plant. Retention was above 90% for the hormones, not being influenced by the pH of the feed solution. The same authors commented that, with the increase in transmembrane pressure from 10 bar to



20 bar, there was a reduction in the retention of micropollutants. Aziz and Ojumu [17] reported that the use of reverse osmosis membranes in the treatment of municipal effluents containing steroid hormones was efficient, with retention percentages above 95% for the micropollutants tested.

Thus, the present work aimed to assess the efficiency of reverse osmosis in the removal of the synthetic steroid hormones ethinylestradiol and levonorgestrel present in aqueous matrices.

Experimental Section

Preparation of feed solution

Synthetic solutions containing the steroid hormones ethinylestradiol and levonorgestrel were prepared for the experiments. These were obtained as commercial contraceptives pills (Ciclo 21®, União Química, Brazil), each pill containing 150 μ g of levonorgestrel and 30 μ g of ethinylestradiol, in addition to the excipients, which were diluted in distilled water [18].

To determine the optimal concentration to be used, a preliminary test was carried out using a contraceptive solution with a concentration of approximately $1.0 \text{ g} \cdot \text{L}^{-1}$, from which the total soluble and suspended solids contents were determined. With this, it was possible to determine the better concentration to be used so the results of the experiments would be within an adequate reading range (within the limits of quantification). In addition, the content of suspended solids and the need for pre-treatment of the solution could also be assessed.

After the preliminary test, the approximate concentration of 1.0 $\text{g}\cdot\text{L}^{-1}$ of contraceptive was selected, the synthetic solution made with the medicine pills, which were weighed on an analytical balance, macerated with a mortar and pestle, and diluted in distilled water.

The reverse osmosis membrane selected for the tests had a flat spiral configuration and tangential flow, composed of polysulfone with a selective polyamide layer, model TFC-2002-100G, manufacturer Metagoal® (Brazil). The membrane was dense and had a surface area of 0.35 m^2 , with a length of 20 cm. According to technical specifications, the maximum operating temperature and pressure of the membrane were 45 °C and 10 bar, respectively.

As the adopted contraceptive has excipients that have little solubility in water, the feed solution containing the hormones had a high content of suspended solids, which precipitate easily. Thus, a preliminary treatment was carried out by vacuum filtration, using qualitative filter paper, for the separation of the suspended solids, thus preventing the presence of suspended solids from interfering with the performance of the membrane. The content of suspended and dissolved solids in the feed solution after vacuum filtration was also determined.

Reverse osmosis tests

After the preliminary vacuum filtration step, reverse osmosis tests were carried out, in which the system configuration shown in Figure 1 was used.



Figure 1. Scheme of the reverse osmosis system used in the experiments.

Initially, membrane compaction tests were performed. For this, transmembrane pressures higher than the operating system pressure were applied until the flow of water became constant. With this, consolidation of membrane structure occurs, preventing this structural variation from occurring during the reverse osmosis tests. For that procedure, 10 L of distilled water was placed into the feed tank and kept at room temperature (20–25 °C). Transmembrane pressure was increased to the system limit (6 bar). Water was kept recirculating for the time necessary until the flow was constant and the system had reached operational equilibrium, as proposed by Baldasso [19].

Determination of the hydraulic permeability of the membrane

Initially, tests were carried out using distilled water to determine the resistance of the membrane to the permeation of the aqueous solution and the fluxes obtained with the pressure variations. For this, the direct volumetric method was used, which consists of calculating the flows from the measurement of the time that the water takes to fill a determined volume [19]. In that test, pressures between zero and 6 bar were used, with intervals of 1 bar every 5 min, at room temperature (20–25 °C). The procedure was repeated for the samples containing the synthetic hormones.

Transmembrane flux data were collected in triplicates, with the data plotted against transmembrane pressure. The data were fitted to a first-degree equation, with the angular coefficient of the regression being the hydraulic permeability of the membrane.

Removal of hormones by reverse osmosis

In the tests with the synthetic solutions, the pressure and the flow were varied in an analogous way to the permeability test with distilled water, being the permeate flux evaluated over time and, posteriorly, the concentration of the hormones ethinylestradiol and levonorgestrel in the feed and permeate streams.

The calculation of the total retention percentage (R) was carried out using Equation 1.

$$R(\%) = 100 \times \left(1 - \frac{C_p}{C_f}\right) \tag{1}$$

Where C_f corresponds to the concentration of hormone in the feed solution and C_p corresponds to the concentration of hormone in the permeate stream, both expressed in milligrams per liter.

Membrane cleaning

Between reverse osmosis tests, chemical cleaning of the membrane was performed to remove possible suspended material remaining in the feed solution, as well as hormones that could adhere to the membrane. The membranes underwent acid cleaning (0.080 M citric acid, pH 2) and alkaline cleaning (0.025 M sodium hydroxide, pH 12), being rinsed with distilled water between each step and at the end of the cleaning process. Each cleaning step lasted 30 min and was performed at 30 °C, as proposed by Zelinski et al. [20].

After each cleaning process, the measurement of the hydraulic permeability of the membrane was performed with distilled water to ensure that the membrane had an efficient cleaning, without its permeability being compromised by the tests.

Analytical method and experimental design

For the quantification of hormones in the feed and permeate samples, the gravimetric method was used, according to the methods described by the Standard Methods for Examination of Water and Wastewater [21], whose quantification limit for the determination of total suspended solids and total dissolved solids was 12 mg·L⁻¹.

The experiments followed a completely randomized experimental design, with three repetitions per treatment. Hydraulic permeability data and transmembrane flux data were statistically evaluated by Analysis of Variance (ANOVA) and the means were compared by Tukey's multiple range test at a 5% probability of error, using the Statistica 12 software (StatSoft, USA).

Results and Discussion

Feed solution and preliminary vacuum filtration step

By evaluating the prepared feed solution, it had $0.15 \text{ g}\cdot\text{L}^{-1}$ of suspended solids, which corresponded to 8.0 wt.% of suspended solids from part of the inert ingredients that make up the contraceptive pills. The concentration of dissolved solids in the feeding solution was $0.96 \text{ g}\cdot\text{L}^{-1}$, totaling 92% of the composition of the contraceptive pills and containing, among other components, the hormones ethinylestradiol and levonorgestrel.

The vacuum filtration step with qualitative paper aimed to remove part of the components of the feed solution, to avoid causing damage to the operation of the reverse osmosis system, such as the formation and intensification of fouling. The results showed that this step retained approximately 9.4% of the material initially present in the feed solution (total suspended solids content below the quantification limit – $12 \text{ mg} \cdot \text{L}^{-1}$), corresponding to the suspended solids present in the composition of the pills.

Assessment of membrane hydraulic permeability

From the measurement of the permeate flux as a function of the transmembrane pressure variation, it was possible to obtain the characteristic curve before the reverse osmosis tests, whose behavior is shown in Figure 2.

It can be observed, by the equation of the linear regression line, that the hydraulic permeability of the membrane, corresponding to the angular coefficient of the regression curve, was approximately 2.24 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$. It can also be noted a mostly linear behavior between the transmembrane flow and the applied pressure, with a coefficient of determination (R^2) of 0.97.



Figure 2. Permeate flux as a function of transmembrane pressure applied to distilled water permeation before reverse osmosis tests.

Permeability values in the range of up to $5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ are characteristic of reverse osmosis membranes, considering that this type of membrane is dense, and the sorption-diffusion mechanism is responsible for the process of separation. Thus, the transport of permeant substances is limited by their sorption through the membrane and their subsequent diffusion

within the membrane structure. Bearing in mind that these phenomena occur more slowly when faced with hydraulic retention promoted by differences in pore size, lower values of transmembrane flux and, consequently, of hydraulic permeability are observed [22].

Similar values of hydraulic permeability were reported in the studies of Martins [23], Rosa [24], and Couto [25], in which the hydraulic permeability found for reverse osmosis membranes was 2.80 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$, 1.01–1.22 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$, and 1.60–2.57 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$, respectively. In cases where the hydraulic permeability has very high values (above an order of magnitude), degradation effects or microruptures of the membrane may likely have occurred. In these cases, this can mean smaller retention through the membrane, decreasing its efficiency and the reverse osmosis process as a whole.

After passing the synthetic contraceptive solution through the membrane, it was observed that there was an alteration of flux behavior relative to the transmembrane pressure, as shown in Figure 3.



Figure 3. Permeate flux as a function of the transmembrane pressure applied to the permeation of a feed solution containing 1.0 $g \cdot L^{-1}$ of contraceptive.

It can be noted that the membrane permeability value after the reverse osmosis process of the contraceptive solution reduced to 2.08 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$, corresponding to a 7.14% reduction in the hydraulic permeability of the membrane compared to before reverse osmosis. This demonstrates that reverse osmosis was effective in removing compounds dissolved in the solution, which were retained in the membrane and, consequently, reduced its flow. However, this retention of dissolved material by the membrane can be detrimental in terms of reducing the separation efficiency by reducing the permeate flow, especially when this reduction is pronounced [26].

Furthermore, it can be seen that the regression curve obtained showed slightly lower linearity ($R^2 = 0.98$) compared to that based on distilled water permeation data. This phenomenon may be due to the formation of fouling, which obstructs membrane pores and make flux values change, generating this discrepancy in the proportionality between pressure and transmembrane flux [20].

Permeation tests were carried out after the chemical cleaning step of the membrane, using only distilled water. The behavior of the transmembrane flux as a function of the applied pressure is compiled in Figure 4.



Figure 4. Permeate flux as a function of the transmembrane pressure applied to the permeation of distilled water, after the chemical cleaning process of the membrane.

After the reverse osmosis experiments and chemical cleaning of the membrane, it was observed that transmembrane fluxes and hydraulic permeability returned to values close to those observed before the tests, indicating that the chemical cleaning process of the membrane was efficient. Thus, the acid and alkaline chemical cleaning steps and rinsing with distilled water removed the adhered material, indicating that this cleaning process can be used in the treatment of membranes after the permeation of this type of feed. Zelinski et al. [20] reported that this cleaning procedure was also effective for this same type of membrane after the reverse osmosis process of galvanic effluents.

Table 1 compiles the average hydraulic permeability and transmembrane flux values at a pressure of 6 bar for each of the study stages.

Table 1. Average hydraulic permeability (L_p) of the reverse osmosis membrane and transmembrane flow (J) at the pressure of 6 bar for the different stages of the study.

Stage	$\begin{array}{c} \mathbf{L}_{\mathbf{p}} \\ (\mathbf{L} \cdot \mathbf{m}^{-2} \cdot \mathbf{h}^{-1} \cdot \mathbf{bar}^{-1}) \end{array}$	J at 6 bar $(L \cdot m^{-2} \cdot h^{-1})$
Distilled water permeation	2.24±0.33ª	13.17±0.87 ^a
Permeation of contraceptive solution	$2.08\pm0.30^{\text{a}}$	11.97±0.84 ^b
Permeation of distilled water post-cleaning	$2.22{\pm}0.20^{a}$	13.20±0.44 ^a
Coefficient of variation (%)	21.11	18.64

Means in column followed by the same lowercase letter do not differ statistically by Tukey's test at a 5% probability of error.

As can be seen in Table 1, the hydraulic permeability was not affected by the reverse osmosis of the contraceptive solution, probably due to its low concentration $(1.0 \text{ g} \cdot \text{L}^{-1})$ in

the feed stream. On the other hand, the transmembrane flow at 6 bar was reduced by approx. 9% during the reverse osmosis process of the drug-containing feed solution. However, the flow was restored after the chemical cleaning procedure.

With that, it can be noticed that chemical cleaning was efficient in removing the compounds adhered to the membrane by restoring the initial transmembrane flux (before assays with the contraceptive-containing solution). The flux may have been reduced during the reverse osmosis tests due to interference phenomena, such as fouling and concentration polarization, in which there is the formation of a solute layer on the surface and in the pores of the membrane during permeation [22]. During system operation, part of these solutes can be pushed into the pores, characterizing a fouling more intrinsic to the membrane and not so shallow, which is more difficult to be reversed, and may even be irreversible [22,27]. However, it can be assessed that the fouling observed in this study was of the reversible type, as the hydraulic permeability of the membrane was not reduced, and the transmembrane flux was restored to the initial condition after cleaning.

In Figure 5 are compiled the graphs of hydraulic permeability as a function of the applied transmembrane pressure, for each of the stages of the study.

The hydraulic permeability as a function of pressure in all experiments had a linear behavior, although with a considerable deviation (R^2 varying between 0.706 and 0.862). This indicates the presence of fouling or other mechanisms associated with reduced sorption and diffusion capacity of the membrane. This phenomenon is most likely the result of the formation of a film of inert material (dissolved solids) on the surface of the membrane, impairing water sorption and, consequently, its diffusion through the membrane, even after the chemical cleaning steps [28].

Concentration of contraceptive hormones in solution

After vacuum filtration, a sample of the solution, corresponding to the feed solution of the reverse osmosis system, was sent for quantitative analysis of total suspended and total dissolved solids. According to the results of the analyses, the feeding solution had a concentration of total suspended solids below the limit of quantification of the method (12 mg·L⁻¹) and a total dissolved solids concentration of 0.814 g·L⁻¹.

In the permeate sample collected after the reverse osmosis process, the concentration of total suspended solids was below the limit of quantification, like the one observed in the feed stream. The concentration of total dissolved solids was reduced to 0.044 g·L⁻¹. From this result, it can be seen that, from the 2.0 g of contraceptive added to distilled water to form the initial feeding solution, containing 1.0 g·L⁻¹ of contraceptive, only 0.088 g remained after the entire treatment process. This represents a removal of 95.6% of the compounds present in the drug by vacuum filtration associated with the reverse osmosis process.



Figure 5. Behavior of the hydraulic permeability of the reverse osmosis membrane in the permeation of distilled water (A), in the permeation of a feed solution containing $1.0 \text{ g} \cdot \text{L}^{-1}$ of contraceptive (B) and in the permeation of distilled water after the cleaning procedure (C).

Similar results regarding the percentages of removal of steroid hormones from aqueous solutions using reverse osmosis are found in the literature, as in the works of Nghiem et al. [15], Koyuncu et al. [29], and Silva et al. [16], cited before, with retention percentages varying in the range of 90.0 – 99.9 %, depending on the adjustment of process parameters, such as pressure, temperature, the composition of the feed solution, and feed flow.

One factor that also has to be considered is that the membrane used in the experiments has already been used in other experiments, not being brand new and possibly having limitations related to possible damage during its previous use or the presence of pre-existing fouling, which may have been potentiated during the reverse osmosis process of the contraceptive solution.

It is not possible to determine the exact composition of the solutions by the gravimetric method. Thus, the compounds that passed through the membrane could either be steroid hormones or drug excipients, which are composed of lactose, povidone, microcrystalline cellulose, sodium lauryl sulfate, croscarmellose sodium, and macrogol [18].

Analyzing the chemical formula of the drug components, it is noted that lactose and the two hormones, levonorgestrel, and ethinylestradiol, have the biggest molecular weights, with 342 Da, 312 Da, and 296 Da, respectively, being more easily retained by the membrane, while the other components, having lower molecular weights, are more likely to cross the membrane and pass into the permeate stream [30]. Another factor to be considered is that lactose is the main carrier of the hormones present in the pills. Considering that this substance is likely to be retained by reverse osmosis membranes, it is expected that the steroid hormones have also been removed from the solution [2,15].

In addition, the compounds croscarmellose sodium and macrogol, inert components of the drug, can polymerize and form extensive chains, with a greater propensity to be removed from the solution and/or encrust the membrane [31]. Regarding drug component solubility, steroid hormones are insoluble in water, which facilitates their separation by reverse osmosis membranes, while other components are partially or completely soluble in water, which makes it easier to pass to the permeate stream [30,32].

Conclusion

Based on the results, it was possible to observe that the process of reverse osmosis, associated with vacuum filtration as a previous step, was efficient in the removal of components of contraceptive pills from aqueous samples, with a retention percentage of 95.6%. There was no reduction in the hydraulic permeability of the membrane, indicating that the formation of fouling or other interference was small. Furthermore, standard chemical cleaning was sufficient to remove the fouling formed during reverse osmosis. Considering that currently there is no specific legislation for the limit of residues of steroid hormone in consumption waters, reverse osmosis presents itself as a valid and interesting alternative for implementation in water and effluent treatment systems since the current treatment processes have low efficiency in removing these micropollutants.

Authors Contribution

D. C. Vanni: Conceptualization, Investigation, Writing-original draft; W. P. Silvestre: Methodology, Formal analysis, Investigation, Writing; review and editing, Visualization; C. Baldasso: Conceptualization, Methodology, Writing; review and editing, Supervision, Project administration. All authors have approved the final version of the manuscript.

Conflicts of Interest

The authors have declare no conflicts of interest

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