

Hormones Nanofiltration in Carbon Nanotubes and Boron Nitride Nanotubes Using Uniform External Electric Field Through Molecular Dynamics

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Hormones are a dangerous group of molecules that can cause harm to humans. This study based on classical molecular dynamics proposes the nanofiltration of wastewater contaminated by hormones from a computer simulation study, in which the water and the hormone were filtered in two single-walled nanotube compositions. The calculations were carried out by changing the intensities of the electric field that acted as a force exerting pressure on the filtration along the nanotube, in the simulation time of 100 ps. The hormones studied were estrone, estradiol, estriol, progesterone, ethinylestradiol, diethylbestrol, and levonorgestrel in carbon nanotubes (CNTs) and boron nitride (BNNTs). The most efficient nanofiltrations were for fields with low intensities in the order of 10–8 au and 10–7 au. The studied nanotubes can be used in membranes for nanofiltration in water treatment plants due to the evanescent field potential caused by the action of the electric field inside. Our data showed that the action of EF in conjunction with the van der Waals forces of the nanotubes is sufficient to generate the attractive potential. Evaluating the transport of water molecules in CNTs and BNNTs, under the influence of the electric field, a sequence of simulations with the same boundary conditions was carried out, seeking to know the percentage of water molecules filtered in the nanotubes.

Keywords: Nanofiltration, Endocrine Disruptors, Molecular Dynamics, Steroid Hormones.

1. INTRODUCTION

Much of the planet's surface is covered by water, but only 3% of it is drinkable. Water resources are reduced by over-fishing, pollution, climate change, and, in recent decades, by the contamination of soils and water bodies [1]. Many hormones have been detected in wastewater [2],

surface [3], and underground [4] in various regions around the world in concentrations from nanograms to micrograms per liter [5]. These pharmaceutical products are being used more and more, and many of these compounds are bioactive chemicals [6] which, once in the environment, can compromise the quality of water resources, biodiversity, and the balance of aquatic ecosystems [7, 8]. Some hormonal drugs, such as estrogens and progesterone

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are considered emerging contaminants [9], and research has yet to determine their effects on human health. Also, there are no laws that regulate the level of these compounds in the environment [10–12]. These hormones are considered endocrine disruptors (ED) and negatively affect the endocrine system in humans and most aquatic organisms [13]. Previous research on aquatic organisms has described reproductive disorders resulting from the presence of estrogens in the environment [14, 15]. EDs are environmental pollutants that persist in treated water and are harmful even at very low concentrations. Domestic sewage generates effluents highly contaminated with substances that are naturally excreted or discarded as hormones and synthetic substances such as drugs [16].

Hormones not removed from sewage treatment plants (STS) will contaminate both the environment and living beings that use contaminated water. The EDs studied are estrone (E1) [17], estradiol (E2) [18], estriol (E3) [19], progesterone (PGR) [20], ethinylestradiol (EE2) [21], levonorgestrel (LNG) [22] and diethylbestrol (DES) [23], but among them, EE2 is considered the most aggressive hormone in the environment. The concern to provide clean water requires new technologies to remove emerging traces of microcontaminants (EMC) that reach wastewater, including steroid hormones that cause progressive damage to the environment, serious diseases, mutations, and infertility [24]. The molecular structures of the seven female hormones (E1, E2, E3, EE2, PGT, LNG, and DES) were obtained from the Protein Database (PDB) (Fig. 1) [25].

The trapping of particles in an evanescent field occurs when the moment of the opposing beams is canceled [26], allowing stable trapping in two dimensions at the interface. Evanescent wave captures applications include particle

transport and classification [27]. The optical link interactions between nearby particles can have significant effects on the observed effects. This can be particularly prominent due to the large size of the capture/transport beam [28]. The optical connection of small microparticles in an evanescent wave trap. This work aimed to study the molecular dynamics (MD) of nanofiltration (NF) of seven female hormones in water, using carbon nanotubes (CNTs) and single-walled boron nitride (BNNTs), activated by eight electric fields (EF) with different intensities, whose results show that it is possible to create systems to filter natural and synthetic hormonal molecules under the uniform action of EF, aiming to obtain drinking water free of hormonal contaminants.

2. REVIEW

Most ED molecules that remain in low concentrations in wastewater are biologically active molecules and living organisms interfere with the synthesis, secretion, transport, binding, action, or elimination of natural hormones [29]. Most substances that act as ED are drugs such as painkillers [30], anti-inflammatories [31, 32], antibiotics [33, 34], antidepressants [35, 36], chemotherapy, and the synthetic hormonal group [37, 38]. The main causes of the increase in the consumption of these drugs are the growing need for hormone replacement [39]. When living organisms ingest surface or drinking water that contains traces of the hormones, they circulate in the plasma and are recognized by the cells of Organs target organs of the hormone, which have receptors on the cell nucleus membrane [40]. Together with hormone receptors, these invasive molecules now command synthesis, secretion, production, distribution, and all endocrine activities.

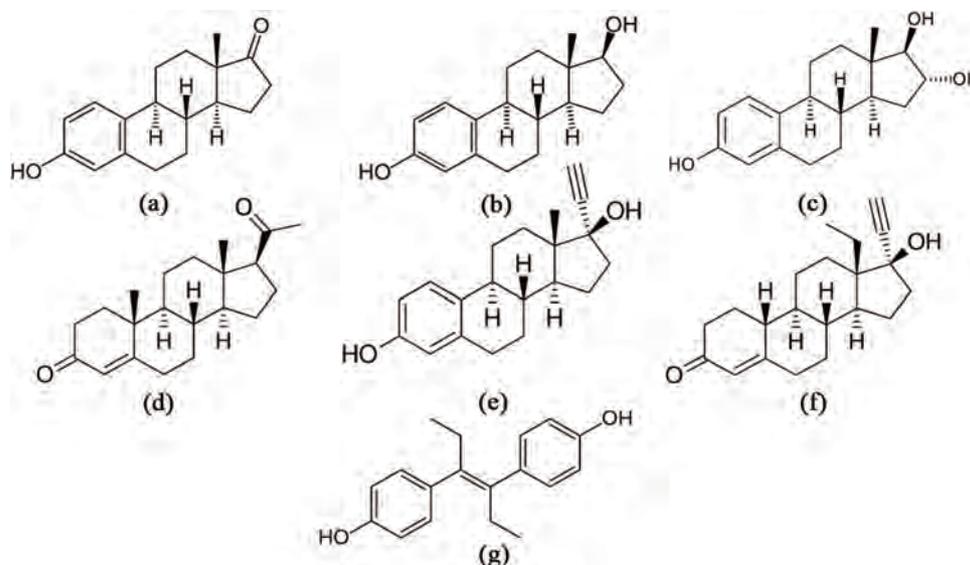


Figure 1. Natural hormones (a) estrone, (b) estradiol, (c) estriol, and synthetic (d) progesterone, (e) ethinylestradiol, (f) levonorgestrel, and (g) diethylbestrol.

The deleterious action of ED on cells is perpetuated because the body cannot destroy molecules that are not part of its metabolic chain [41, 42].

Among EDs, another group is synthetic substances that mimic estrogenic function, xenoestrogens [43], which can also be natural and synthetic. The natural ones come from plants [44]. In addition to having no harmful effects, they can have a protective effect when circulating in the blood plasma, but synthetic xenoestrogens can occupy the same cellular receptors as the target organs for estrogenic actions [45–46]. Research confirms evidence of metabolic changes caused by ED in marine species [47–48], in animals for slaughter, and vegetables [49]. In humans, hormones that act like ED elevate cases of endometrial cancer [50, 51], prostate cancer [52, 53], cause kidney disorders [54]. Exposure of pregnant women presents childhood obesity with susceptibility to several metabolic disorders [55, 56]. Several systems suffer the action of uncontrolled steroid metabolic pathways, such as the neurological system [57], with behavioral disorders, such as autism [58] diseases occur in the cardiovascular system, bones [59], and liver diseases [60]. Prenatal exposure can alter the shape or functionality of the reproductive system [61, 62] and can cause infertility in humans and other organisms [63, 64].

It is not always possible to estimate the concentration of ED in wastewater. Very low concentrations do not reduce the risk of endocrine disruption; therefore, detecting, treating, and maintaining control to eliminate contaminants is a means of preventing diseases in the population and preserving the environment [65]. NF membranes are still the best method for filtering effluent hormones, but the effectiveness of this technique depends on previous separation processes. The adsorption of organic matter in the pores and surfaces of the nanotubes membranes forms incrustations, which reduces the volume and quality of the NC. The NF membranes that filter the smallest effluent molecules can also serve as an ED reservoir for cleaning and disposing of the water used in this procedure [66, 67]. Nanotubes membranes can be improved to remove ions, but they still need to remove traces of organic contaminants that compromise the reuse of wastewater. Studies have been reported to improve permeability, selectivity, and anti-fouling properties [68–69]. NF simulation studies have demonstrated the effectiveness of particle retention in water desalination and decontamination research, certainly due to the ease of the water diffusion process at CNTs [70, 71]. When EF is applied, the transport of molecules in the NT causes an increase in the electrostatic forces of the entire system and recommends a greater demand for studies to understand the dynamics of the NT interacting with the molecules that pass through it [72]. EF is an essential phenomenon for improving the transport of molecules [73]. The kinetics of water molecules in different states within an NT showed in simulation studies that electrostatic interactions or hydrogen bonds in the

nanotube armchair structure are more intense in the presence of an EF [74, 75]. The NF ϵ which is influenced by the translocation time is directly related to the temperature when high, influencing the dipole and the density of the water [76, 77].

The pore diameter of CNTs and BNNTs constitute barriers to the NF of organic molecules and the single-walled nanotube in the armchair conformation [78], has excellent electrical current conduction properties at room temperature, having already been tested in electrochemical filtration with good performance. The applied EF induces the hydrophilic nature of the nanotubes, facilitating the transit of water molecules that tend to orient themselves towards the positive pole due to electronegativity the water molecules have partial negative charge next to the oxygen atom, because of the pairs of unshared electrons, and has partial positive charges next to the hydrogen atoms. The interactions of hormones with water, under an EF, in the NF process can be better understood with the knowledge of chemical, structural and molecular properties that influence the results.

3. METHODOLOGY

To perform the computer simulations of this study, the structures of nanotubes and hormonal molecules were modeled with the most stable conformations. In the modeling step, the classic MM+ method was used for energy optimization and molecular geometry, with the Polak-Ribiere conjugate gradient algorithm [79], to perform the interactive energy minimization cycles individually for each molecular structure. The convergence criterion of the energy gradient was 0.01 kcal/(mol Å). The different types of atoms contained in hormones are attributed to different elements, but also different states of hybridization, generally even for atoms in the same state of hybridization, but in a different chemical environment. The calculations were analyzed for the total time of 100 ps. The molecular mechanics methodology was used in conjunction with the processes and parameterization of force fields and molecules [80]. In this process, electronic correlations were ignored and only the positions of the atoms were considered.

The intermolecular forces in the process can be described in terms of potential energetic functions of structural characteristics, such as connection lengths and angles, non-binding interactions, among others [81]. The combination of these potential energetic functions corresponds to the force field. After the minimization of energy, the conformational analysis [82] of the molecules was carried out, where a systematic search was performed for the values of the dihedral angle of all rotating connections and, thus, finding the lowest energy conformation for each structure. Finally, once the most stable molecular structures were

obtained, the MD calculations were calculated, based on the interaction energy and Newton's equations for motion. MD simulations were performed with the system at an initial temperature of 300 K varying during the simulation and, to verify the effect of EF in the simulations, it was applied throughout the system, parallel to the nanotubes and with constant intensities during each simulation. This occurred in a vacuum, so the nanotubes remained rigid during the simulations, while the other molecules, such as water and hormones, relaxed.

The intensities of the EF varied between 10–1 a.u. and 10–8 a.u. being 1 a.u. = 5.14×10^9 V/cm). Some physical properties were calculated, such as kinetic energy (EKIN), potential energy (EPOT), total energy (ETOT), and system temperature *in situ*. The synthetic and natural hormonal molecules were placed individually in the center of the nanotubes, as shown in Figure 2, together with 100 water molecules and were then exposed to different intensities of uniform and longitudinal EF. CNTs were modeled with 1064 atoms, 91.74 Å in length and 12.59 Å in diameter, and the BNNTs with 1162 atoms, measuring 91.98 Å in length and 12.69 Å in diameter. Various constant values of external EF were applied longitudinally to the nanotubes, along the length of their length, promoting an evanescent effect capable of trapping each molecule and making it rotate around the nanotube with high-speed values and kinetic energy [83]. This simulation was performed using the same methodology proposed by Neto [84] and Guo [85], using the Hyperchem 7.5 [86] software. The MD method calculated the trajectory of the molecules when exposed to different EF values.

The simulation was performed using SPC (Single Point Charge) for the computational efficiency proven in simulations of water molecules that receive parameterization of the force field [87]. The isothermal-isobaric set keeps the number of molecules, the temperature, and the pressure of the system constant. The number of molecules and the simulation time generate high computational costs, therefore, for studies of larger systems, the MD follows the principle of Boltzmann's ergodic hypothesis [88] in which the average value of a property measured in a small number of particles for a long time is equal to the averages obtained for a multiparticle system during a short period [89]. Thus, in the study of MD simulations,

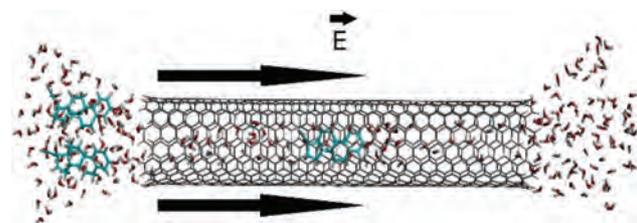


Figure 2. Electric field applied to the longitudinal axis of the CNTs, the water molecules are released while the hormonal molecule is retained.

there must be few molecules, but the trajectories and time were sufficient for the system to obtain a sufficient number of representative conformations that contemplated this principle [90].

3.1. Molecular Electrostatic Potential

The topographic electrical polar surface area of a molecule also serves as a parameter for understanding intermolecular interactions, especially in the case of hormones concentrated in plasma or water [91–93]. In addition to the numerical data, the molecular electrostatic potential (MEP) was calculated, which allows us to see the charge distribution of each hormonal molecule, due to the complexity of its interactions with water. In Figure 3, the MEP's of the studied molecules are shown, where the arrangement of negative charge density at their ends was observed. This same disposition of electronic density was observed as a common characteristic in hormones, which present interactive activity. At MEP knowledge of charge distributions can be used to determine how molecules interact with each other. The MEP was generated using the Gaussian 09 W software [94], the results of which can be viewed with GaussView 06 [95, 96].

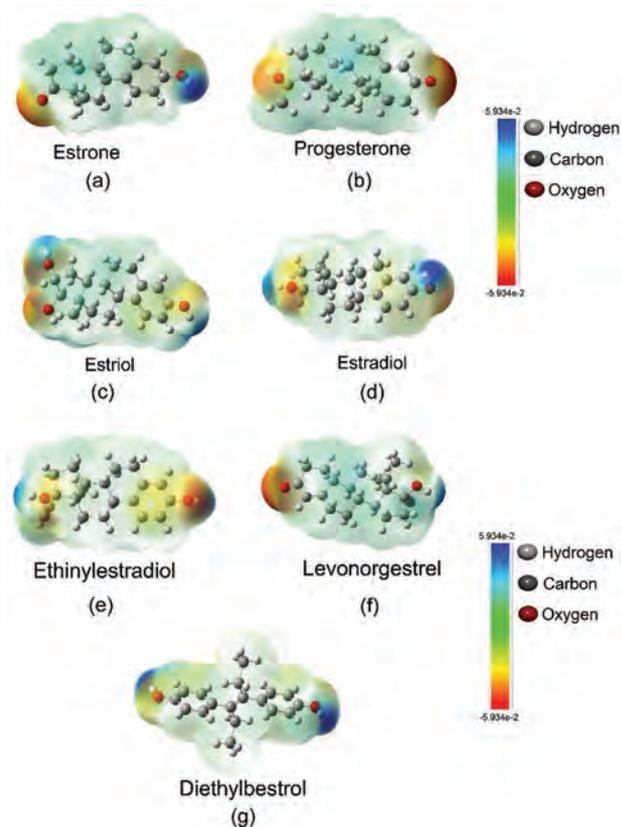


Figure 3. MEP of natural hormones: Natural hormones (a) estrone, (b) estradiol, (c) estrinol, and synthetic (d) progesterone, (e) ethinylestradiol (f) levonorgestrel and (g) diethylbestrol.

4. RESULTS AND DISCUSSION

MEP was also used to analyze processes based on molecular recognition in hormone-nanotube interactions, as it is through their potentials that the interaction strength of the two species can be determined. MEP for electronic density is a very useful property for understanding the site of the electrophilic attack and nucleophilic reactions, as well as the interactions of hydrogen bonds. The MEP at a given point (x, y, z) in the vicinity of the hormones is defined in terms of the interaction energy between the electric charge generated from the electrons and nuclei of the molecule. Among the natural hormones, PGR is the only one that does not have a benzene core, but has a steroid core, like the others. Its functional groups have no electrical polarity, they are two ketones and three methyls. In PGR, the induced dipolar forces of the steroid nucleus prevail because it has the highest atomic mass of the seven hormonal molecules. Thus, progesterone is a nonpolar molecule, more difficult to filter, due to its hydrophobicity and size that exerts a repulsive action on water molecules. Theoretically, we analyzed the surface of the MEP and clearly shows the existence of a region of positive potential above and below the hydroxyl and ketone atoms. The maximum MEP value is located in the OH atoms and the OH and R–C–R atom belts are negative, therefore, suitable to participate in the binding interaction as π acceptors (Lewis base).

In synthetic hormones, EE2 and LNG are analogous to natural hormones E2 and PGR, respectively. EE2 has the same polar electrical area as E2 (a natural hormone that gives rise to synthetic EE2) because it has a similar structure; LNG is a synthetic analog of progesterone, but with the substitution of a ketone group for a hydroxyl, which is a polar electrical group and allows greater interaction with water and other polar electrical liquids. In wastewater, free estrogens join groups of glucuronide, sulfate and form electrical polar compounds that increase the permanence of hormones in the water [97]. The formation of conjugated estrogens represents a potential risk to the environment. DES is a non-steroidal estrogen that has the lowest atomic weight in the group. DES is the only one of the seven hormones that do not have a steroid nucleus but has two benzene nuclei attached to two hydroxyl functional groups. DES has an open central chain and in this geometry the surfaces of interaction with water increase and with functional groups becoming the most hydrophilic molecule in this group. The order of electrical polarity, by functional group, begins with DES, followed by EE2 and LNG. Regarding the polar electrical surface of these molecules, DES and EE2 have the same polar electrical surface, and LNG, the largest molecule in molecular weight has the smallest polar electrical surface in this group.

4.1. Nanofiltration Simulation Using the External Electric Field

The simulations carried out on both nanotubes revealed that the increase in the EF intensity increased the amount of confined water and, therefore, the number of filtered molecules. The walls of the nanotube constitute the simulation box and the force of the uniform external EF acts on molecules that have a permanent charge and dipole, intensified by van der Waals' electrostatic forces. BNNTs is more hydrophobic than CNTs, but both, after the application of EF, confer the hydrophilic characteristic, allowing a better flow of water. BNNTs has better conductivity and thermal stability [98] than CNTs, which directly influences the thermodynamic balance of the system, allowing better results when applied EF. The increase in EF resulted in both NTs in a progressive reduction of the filtered water molecules. Part of these molecules is retained by the evanescent effect that occurs with the increase in EF in electrically charged ions.

The evanescent effect, which results from the strength of EF in water molecules whose van der Waals forces are opposed to EF, giving rise to an electrostatic field called the evanescent field that has the effect of "trapping" molecules inside the nanotubes [99]. The dipole moment of water molecules allows the intensity of EF to influence its flow in one direction. The alignment of the EF-induced water molecules will cause the pre-existing hydrogen bonds to become unstable and break. The balance between hydrogen bonds and van der Waals forces gives rise to dispersed molecular clusters, because EF decreases the lengths of the molecular bonds between oxygen and hydrogen, causing changes in the stability of water molecules, vibrational frequencies, and energy dissociation that influenced the NF.

4.2. Nanofiltration of Natural Hormones

The four natural and two synthetic hormones (EE2 and LNG) have the central structure of the steroid nucleus (or cyclopentanoperhydrophenetrane nucleus) with four cyclic structures (Fig. 4). The steroid ring has 17 carbons that make up the majority of the group's steroid hormones, are nonpolar electrical structures, and have a lower electronic density than water. The difference in the solubility of these molecules in water is made by the size, geometry, and electric polar functional groups that are connected to the steroid nucleus. The hydroxyl and ketone functional groups present in different amounts in the seven hormones in this study are polar electrical groups that can establish hydrophobic interactions with water [100, 101].

The E1, E2, and E3 molecules have similar chemical structures, molecular mass, and geometry, with the same functional groups on carbon 3 and 13. E1, E2, and E3 have a benzene core with carbon hydroxide 3 in the steroid core (C-3). The benzene core contributes to the stability of the molecule by the resonance effect [102, 103]. At carbon 13,

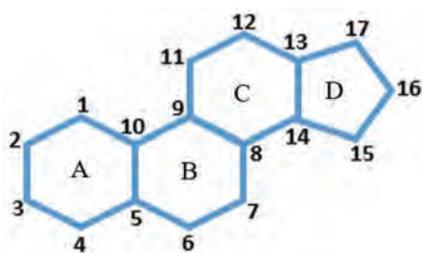


Figure 4. Steroid nucleus or cyclopentanoperhydrophenanthrene nucleus.

the three molecules have a methyl group, not an electric polar. The electronegativity of the hydroxyls' oxygen in contact with the water molecules causes dipole–dipole interaction and a non-symmetric charge distribution occurs in this region (at the same time). This electrical effect polarizes the OH bond so that the hydroxyl hydrogen is positively charged, resulting in an electric dipole moment of the molecule with water that influences the amount of water filtered in the simulation. The size of the hormone molecule also influences the electrical polarity, because when the carbon-hydrogen chain increases, the molecule's hydrophobicity prevails over the functional groups.

The interaction of water molecules with EF changed the transit of water molecules in the simulation, as shown in Figure 5, where the percentage of filtered molecules was reduced. Among the natural hormones, only the PGR has a steroid core without benzene and functional groups with little or no electrical polarity: two ketones and three methyls. In PGR, the electrical dipole forces induced from the steroid nucleus prevail because it has the highest atomic mass of the seven hormonal molecules. Thus, progesterone is an apolar electrical molecule, of greater difficulty and more difficult to filter due to its hydrophobicity and size, which has a repulsive action on water molecules. The similarity in the size of the molecules, in the molecular geometry, and in the number of hydroxyl functional groups of the natural hormones E1, E2 and E3 directly influenced the number of filtered water molecules, the difference in the percentage of filtered water molecules in BNNTs and CNTs, occur due to the influence and distribution of the load on the different types of NT, the third parameter is an important element in all NF results. PGR is the most branched molecule in the central chain of the natural hormonal group. The functional groups of PGR are two ketones that have less electrical polarity than hydroxyls of other organic molecules. Thus, because it is the largest molecule in carbons, the nonpolar electrical characteristic of the central chain of the steroid nucleus prevails. Due to its more complex geometry and functional groups with less electrical polarity, the PGR showed the highest hydrophobicity of the group of natural female hormones and the lowest yield in the NF, of 75% of the filtered water molecules in the CNTs with EF intensity of 10–8 au and 79% in the BNNTs for the EF of e 10–8 au, the functional

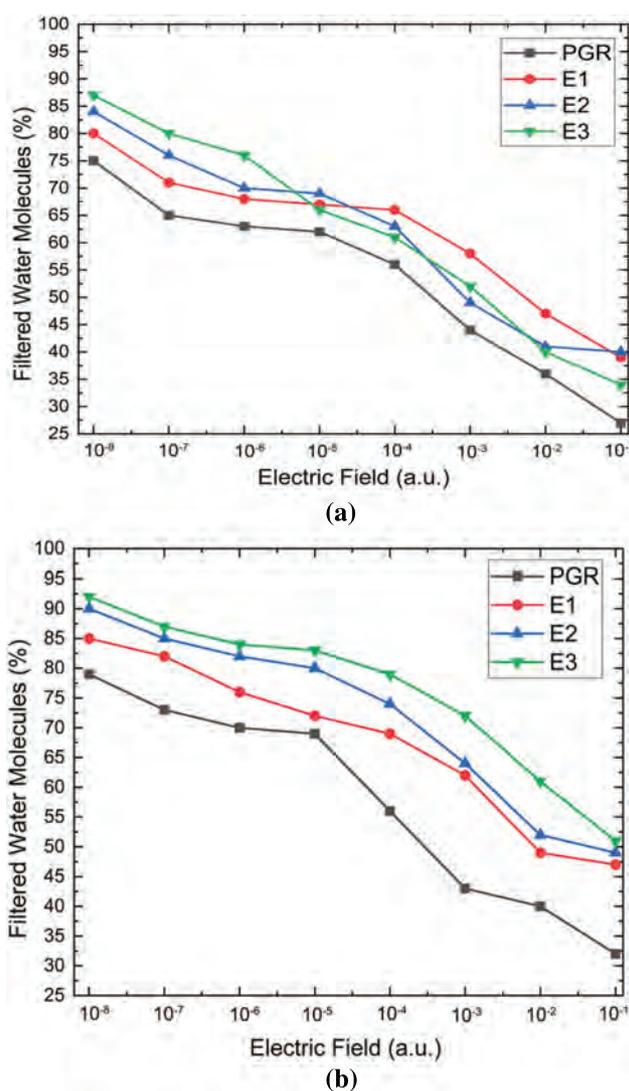


Figure 5. NF representation of natural hormones: (a) CNTs and (b) BNNTs.

ketone group has a permanent intermolecular interaction as an electrical dipole, stronger than the induced electrical dipole present in the atoms of the steroid nucleus, but smaller than the hydrogen bonds established with hydroxyls. Under the effect of EF on CNTs, the pairs of ketones that do not bind to oxygen (4 atoms) interact and establish bonds that stabilize the molecule by resonance. Thus, the interactions of PGR with water molecules occur in a very limited way and this hormone prevails in the characteristics of non-polar electrical central chains (and repels water molecules) [104, 105].

Figure 5 shows that the NF of the four natural hormones in the water, with the best results and the lowest energy expenditure, was related to the smallest atomic mass molecule, E1 which filtered about 89% in EF from 10–7 au in the CNTs and 90% in EF from 10–8 au at BNNTs. Of the hormones E2 and E3, the NF released 84% and 87% of the water molecules, respectively, in the CNTs,

while in the BNNTs the E2 and O3 released 87% and 93% of the water molecules, respectively, for the 10^{-8} au. The synthetic hormone EE2 is homologous to the natural hormone and has the same molecular structure as E2 with the addition of the radical estradiol to carbon 17 [106, 107]. Ethinyl is an alkyl group that has free valence in a saturated carbon and its nonpolar electrical characteristic allows only induced interactions by the dipole. Among natural hormones, only the PGR has a benzene-free steroid nucleus and functional groups with little or no electrical polarity: two ketones and three methyls. In PGR, the electrical dipole forces induced from the steroid nucleus prevail because it has the highest atomic mass of the seven hormonal molecules. Thus, progesterone is an apolar electrical molecule, more difficult to filter due to its hydrophobic property and size, which has a repulsive action on water molecules.

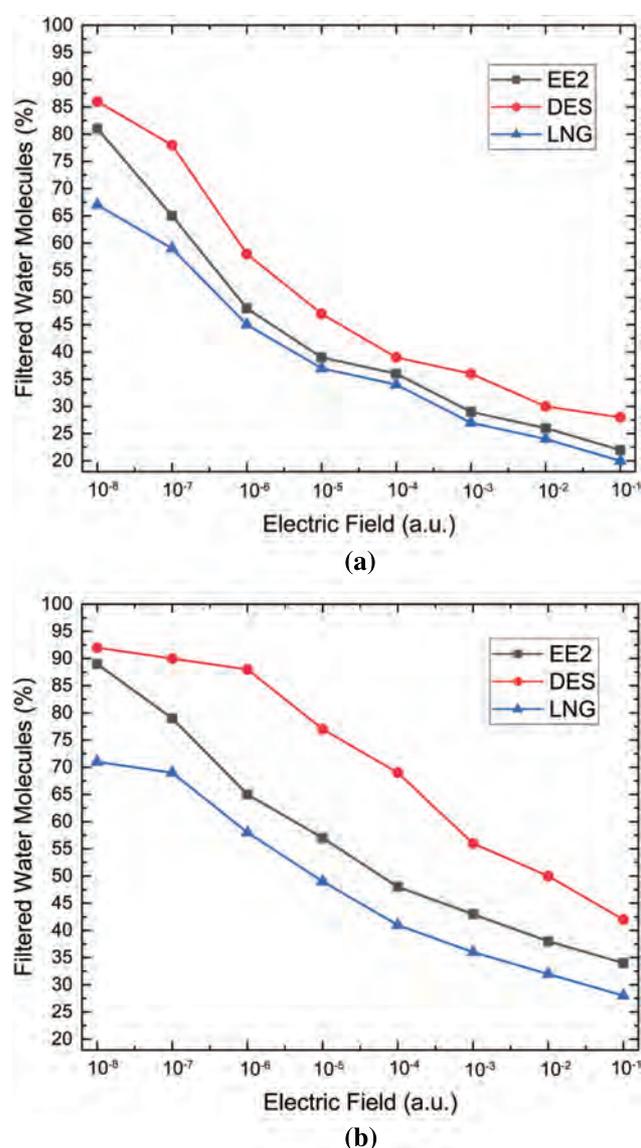


Figure 6. NF of synthetic hormones: (a) CNTs and (b) BNNTs.

4.3. Nanofiltration of Synthetic Hormones

NF at EF of 10^{-8} a.u. made it possible to expel 80% of the water molecules with LNG to the CNTs and 90% to the BNNTs. The nanotubes with EE2 obtained the lowest values for the lowest EF intensity, in both nanotubes with values close to the percentage of molecules expelled in 72% for CNTs and 71% for BNNTs. The DES molecule obtained better filtration of water molecules in both NT 86% and 93% expulsion for CNTs and BNNTs as in Figure 6. Synthetic PGR is the largest molecule among synthetic hormones in several atoms and molecular mass. It has two functional groups at the extremities: a ketone and a hydroxyl, with the electrical apolar characteristic of the predominant molecule [108, 109]. The natural hormone has two ketones as an electrical group. In the comparison between LNG and PGR, the data reveal that, for synthetic hormones, the highest release of water molecules was obtained at the lowest EF value, as a result, as the intensity of the EF increased the NF in the two species of NT decreased.

There was a better yield of NF in BNNTs because although both NTs are hydrophobic, the chemical constitution of BNNTs increases its degree of hydrophobicity, which contributed to the expulsion of more water than in CNTs. The influence of EF on water dynamics, generates flows inversely proportional to the increase in EF, are well established in these conditions, just as the propelling effect of water in the transport of molecules within the NT is related to the size, chemical structure, and electrostatic potential of the molecules to be filtered.

5. CONCLUSIONS

The criterion for comparing the relative stability of the NF in this work was the ease of the NF of water molecules when they are under the action of different intensities of EF. Our data showed that the action of the EF in conjunction with the van der Waals forces is sufficient to generate attractive potential within the NT. This system demonstrates the potential to be used as an efficient CNTs when exposed to a longitudinally directed EF. The NF study using the female hormones MD in the water revealed that EF between 10^{-8} a.u. applied in successive stages of the NF can contribute to the removal of the natural hormones E1, E2, E3 and PGR EE2, LNG, and DES. The filtering of natural and synthetic female hormones in EF-activated NTs is indicated for the removal of female hormones that persist in low concentrations in wastewater from sewage treatment plants.

BNNTs have excellent thermal stability and better filtration, as shown in Figures 5(b) and (b), boron can also form monoatomic leaves and can be used to obtain greater thermal stability in NF processes. After using MD to simulate the behavior of the hormones inserted in the CNTs and BNNTs, for different EF intensity values, and with that, it is possible to infer that the technique presented

in this work seems to be effective, regarding the NF and that, this process it occurs due to the effect of an evanescent attractive potential in the interior. Thus, both species of NTs could be expressed and used in membranes for NF in water treatment plants due to an evanescent field potential within NTs, our data showed that the action of EF in conjunction with van der Waals' forces nanotubes is enough to generate attractive potential. Both nanotubes, which have hydrophobic potential and very narrow diameters, can represent a simplified model of the channels of these membranes, reproducing these critical characteristics in a simpler and more robust platform. New water simulation studies with a greater number and diversity of organic molecules (in addition to hormones) are needed to apply NF to CNTs and BNNTs, as a sequential process of ultrafiltration in the separation of effluents. Experimental studies should confirm whether EF activated NF in NT could replace or augment current NF systems with organic/inorganic membranes.

Data Availability

The data used to support this study is included in the article.

Authors' Contribution

All authors designed and developed the study. All authors read and approved the final version of the manuscript.

Conflicts of Interest

The authors declare that there is no conflict of interest in the publication of this article.

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