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ESTROGEN REMOVAL FROM WASTEWATER

USUWANIE ESTROGENU ZE ŚCIEKÓW

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Abstract

Currently, a significant problem of water and sewage management is the presence of human hormones, especially estrogens and progestagens, consumed by women in contraceptives and then excreted from the body. While other drugs are used by a small part of the population and rather sporadically, hormonal contraception is used by a large number of women, which contributes to their high concentration in sewage. Even relatively low estrogen concentrations (compared to other drugs) can have harmful effects on the body, disturbing the hormonal balance and leading to various endocrine disorders. In this paper the types of individual estrogen groups were characterized. Next, different methods of their removal from wastewater were presented. The parameters of estrogen removal efficiency depend on which parameters. Next, the effectiveness of each method was compared, also taking into account economic aspects. The work was summarized with appropriate conclusions.

Keywords: estrogens, hormones in sewage, methods of estrogen removal from sewage, sewage treatment

Streszczenie

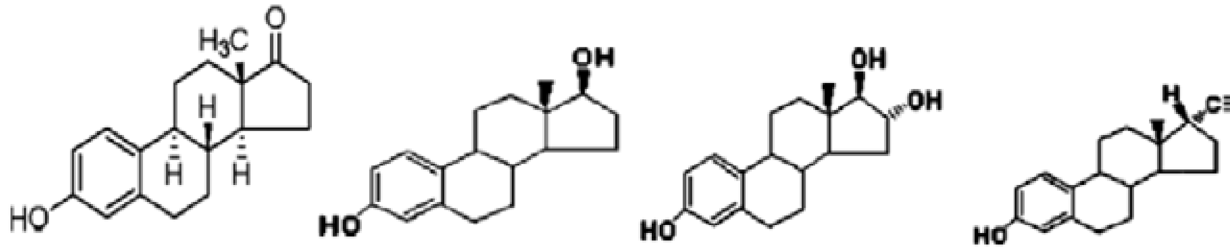
Obecnie istotnym problemem gospodarki wodno-ściekowej jest obecność w ściekach ludzkich hormonów, a zwłaszcza estrogenów i progestagenów, spożywanych przez kobiety w preparatach antykoncepcyjnych i wydalanych następnie z organizmu. O ile po inne leki sięga niewielka część populacji i to raczej sporadycznie, o tyle z antykoncepcji hormonalnej korzysta olbrzymia liczba kobiet, co przyczynia się do wysokiego ich stężenia w ściekach. Nawet stosunkowo małe stężenie estrogenów (w porównaniu z innymi lekami) może mieć szkodliwe skutki dla organizmu, zaburzając w nim równowagę hormonalną i prowadząc do różnych schorzeń endokrynologicznych. W pracy scharakteryzowano rodzaje poszczególnych grup estrogenów. Następnie przedstawiono różne metody ich usuwania ze ścieków. Przedstawiono, od jakich parametrów zależy efektywność usuwania estrogenów. Następnie porównano skuteczność każdej z metod, biorąc również pod uwagę aspekty ekonomiczne. Pracę podsumowano odpowiednimi wnioskami.

Słowa kluczowe: estrogeny, hormony w ściekach, metody usuwania estrogenów ze ścieków, oczyszczanie ścieków

1. INTRODUCTION

Natural and synthetic oestrogen groups E1 (ester), E2 (oestradiol), E3 (oestriol) and EE2 (oestradiol) have a very high impact on water and wastewater management, their chemical structure is shown in Figure 1. A large proportion of hormones pass through wastewater treatment systems and are discharged continuously to the environment, mainly to surface water. These compounds are subjected to biotransformation, bioconcrete and potentially bioaccumulate. As a consequence of this behaviour, problems arise for organisms living in water. Due to the fact that surface water is used for the production of drinking water, the problem of estrogen content seems to be important, especially in terms of possible endocrine disruption to humans and animals.

The article presents methods of estrogen removal from sewage. There are two ways to effectively remove estrogens from wastewater. The first is the optimization of existing treatment technology, while the second is the modernization of existing wastewater treatment plants using the new "end of pipe" technology.



Estrone (E_1) 17β-Estradiol (E_2) Estriol (E_3) Ethinyl Estradiol (EE_2)

Fig. 1. Molecular formula of estrogens: estrone (E1), 17β-estradiol (E2), estriol (E3) and ethinyl estradiol (EE2) [1]

2. CONVENTIONAL WASTEWATER TREATMENT

Conventional Wastewater Treatment (STW) is usually a three-stage process comprising an initial stage, i.e. treatment, primary sedimentation and secondary treatment. However, it has already been found that biodegradation and biotransformation of steroids took place in the sewage network, before the inflow to the treatment plant [2]. This is due to the presence of bacterial sludge, which accumulates on the pipe walls, often leading to anaerobic biodegradation. In large catchments, the retention time of the sewage system may be significant, allowing for a high degree of degradation and processing into other compounds [3]. Conventional sewage treatment is the best model to study the mechanisms thanks to which natural estrogens are suppressed in nature and technical systems. It is commonly believed that processing and biodegradation are the two main processes of estrogen removal from wastewater; however, some question that adsorption may play a significant role in estrogen removal. The content of individual estrogen groups in the wastewater flowing into wastewater treatment plants worldwide is shown in Figure 2.

The Figure 2 above shows that most countries are dominated by higher levels of E1 or E3, with the exception of Spain which showed the highest levels of synthetic EE2, which may be due to the high rate of contraceptive use by Spanish women. The high

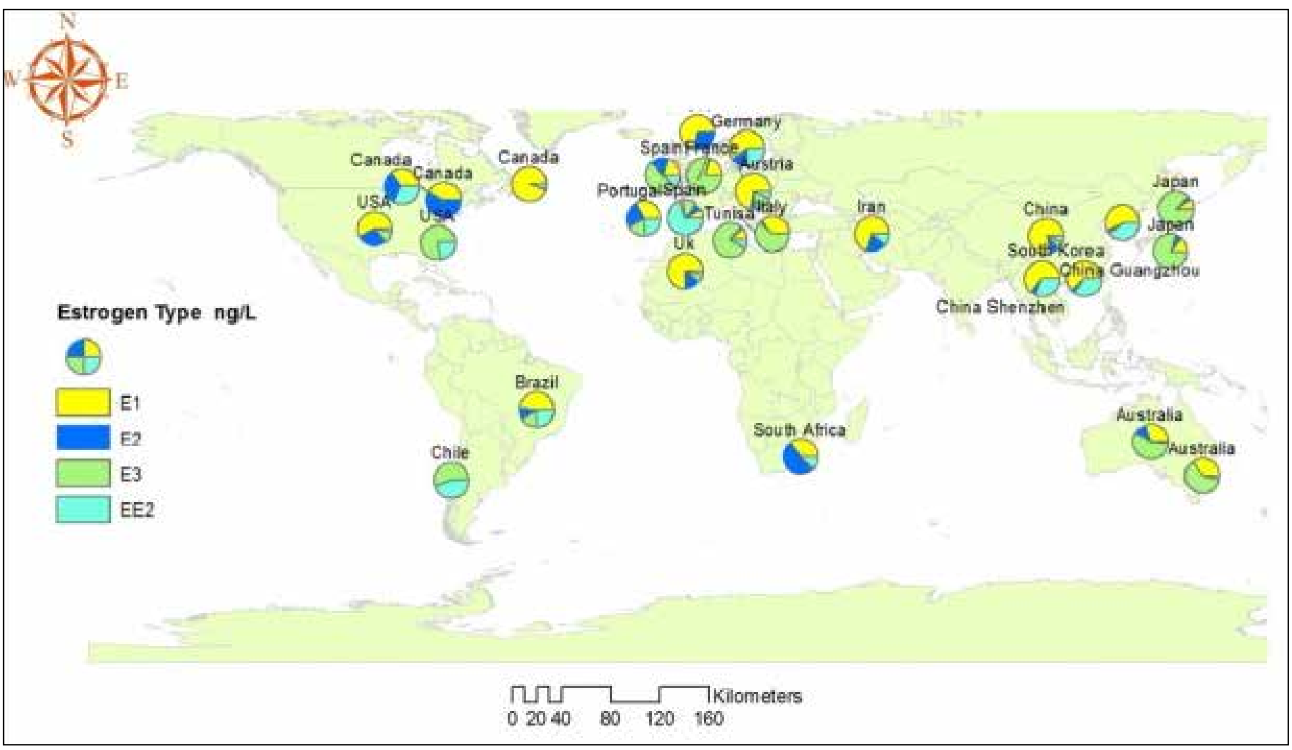


Fig. 2. Worldwide distribution of steroidal estrogens through WWTPs. Each pie chart comprises the natural estrogens: E1, E2, E3 and the synthetic EE2 as percentages [4]

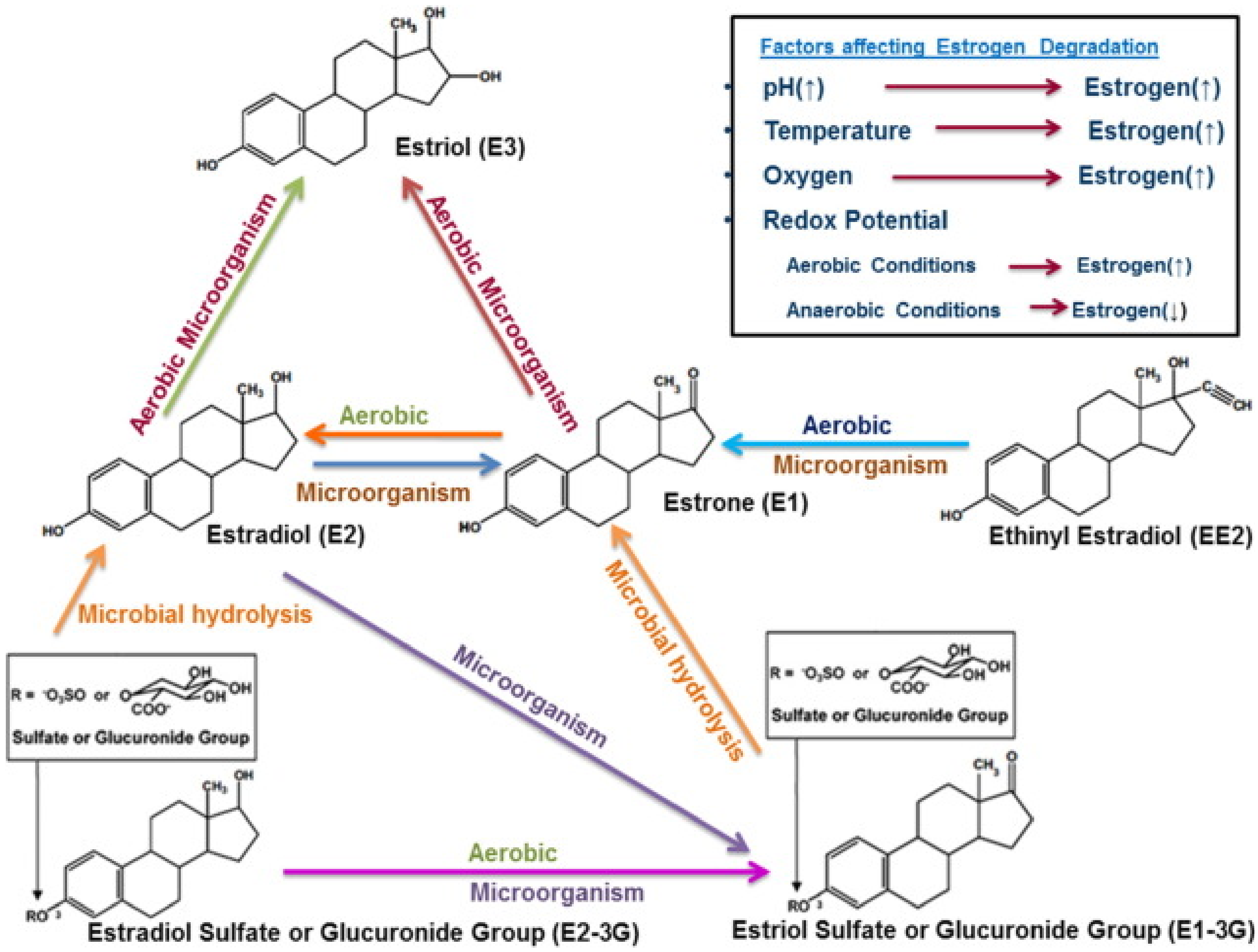


Fig. 3. Interconversion pathways of natural and synthetic estrogens [10]

content of E3 may correlate with high fertility, since it is the hormone mainly produced by pregnant women.

A pregnant woman's organism produces even 120 times more estriol (E3) hormone than a woman's organism during the menopause [5].

As mentioned earlier, estrone (E1), oestradiol (E2) and estriol (E3) lie on interrelated metabolic pathways [6]. Aerobic microorganisms can convert one estrogen into another as shown in Figure 3. For example, some microorganisms (e.g. nitrifying bacteria) can convert E1 to E3 and others decompose E1, E2 and EE2 (e.g. Novosphingobium sp. in the active sediment) [7]. Moreover, synthetic EE2 can be converted to E1 by Sphingobacterium sp. [8]. There is also a diverse range of anaerobic bacteria, which can convert one estrogen into another. For example, in lake water and sediments under anaerobic conditions, E2 was chemically converted to E1 under methanogenic, sulphate, iron and nitrate reducing conditions, but in contrast, no degradation of synthetic EE2 was observed [5, 9].

2.1. Pre-treatment

During mechanical cleaning, larger solids, easily dropping suspensions, oils and fats and granular particles from 0.1mm are removed. During mechanical wastewater treatment processes such as straining, flotation and sedimentation take place. A small amount of organic material is removed from the screens. At this stage the presence of micro pollutants and steroid hormones is observed [11].

2.2. Sedimentation

The sedimentation process consists in the free fall of particles to the bottom under the influence of gravity. The basic criterion required for this process is the difference in density between the fluid and the particles that are suspended in it. In the sedimentation tanks, the mechanism of estrogen removal takes place through adsorption. The degree of micro-pollution removal depends primarily on the hydrophobicity of hormones, content of suspended solids and their subsequent deposition, retention time and surface loads [12].

Lipophilic compounds, such as fats, oils and greases, may be adsorbed by a significant amount of hydrophobic compounds, including many endocrine disrupters, which are removed. Estrogens are hydrophilic, which is indicated by low adsorption [13].

2.3. Secondary treatment process

Secondary biological purification has been shown to be a key process behind the ability of some STWs to remove most or all estrogenic activities. Transformation and biodegradation play a significant role in the removal of hormones, as some microorganisms present in biological STWs have the potential to use steroid estrogen among other micro-pollutants as a source of carbon for metabolism [13]. The fastest and fullest degradation of contaminants present in STW occurs under aerobic conditions through catabolic routes [14].

3. REMOVAL OF STEROID HORMONES BY MEANS OF ACTIVATED SLUDGE

During biological treatment with activated sludge, the impurities in the wastewater are broken down by microorganisms. Due to the life processes of the microorganisms, the pollutants (mostly organic) are broken down. Biological processes are mostly aerobic processes and therefore require a constant supply of oxygen. Microorganisms consume oxygen during their life processes and therefore require a constant supply of oxygen during biological purification; unfortunately, this process is highly expensive. Wastewater from microbial processes is less susceptible to crumpling. In active sludge technology, suspended biocoenosis can be observed, slowly floating in the treated liquid [15].

In a study with active sludge carried out by Bernardelli et al., the concentration of E2 and E1 decreased by about 81.5 and 76.7%, respectively, over 24 h, as shown in Figure 4 [16]. In order to verify the share of adsorption in estrogen removal, the test with inactive sediment was carried out in Figure 4. The concentration of EE2 decreased with time more than the concentration of E1 and E2 (94% in 1 h). This fact resulted potentially from higher hydrophobicity of EE2 (LogKow = 4.1) compared to natural estrogens E1 and E2 (LogKow = 3.1 and 3.4 for E1 and E2 respectively) [17].

The high capacity to remove E2 of activated sludge potentially resulted from various factors, including mechanisms of biodegradation and/or sorption. Thus, Li et al. considered that this estrogen is strongly adsorbed on active sludge particles [16], while other authors indicated that E2 is rapidly oxidized to E1 [18].

4. REMOVAL OF STEROID HORMONES BY MEMBRANE BIOREACTORS

In municipal wastewater treatment, bioreactors with UF/MF membranes are used. Separation of particles from the solution is a sieve mechanism, which means that particles with a diameter smaller than the membrane pores pass through the microporous membrane: in microfiltration (MF) it is 0.1-10 μm in diameter, in ultrafiltration (UF) it is 0.001-0.1 μm in diameter. The most commonly used membranes have pore sizes in the 0.01-0.3 μm diameter range. Membranes in MBR reactors are made of special hollow-fiber hollow fibers with pore diameter of 0.03-0.04 μm [19]. The individual fibres are fixed in packs forming modules immersed in the activated sludge. Filtration takes place from the outside of the tube to the inside using a light vacuum

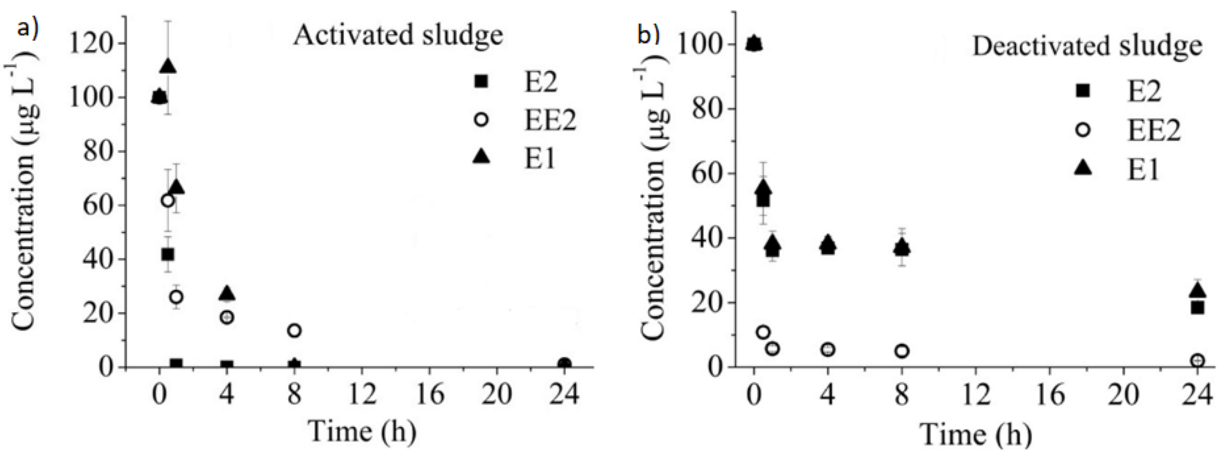


Fig. 4. The removal of estrogens with (a) activated sludge and (b) deactivated sludge (error bars give the standard deviation ± SD). Insert: estrogen concentrations over 24 h [16]

produced by the filtrate pump. The membranes can be installed in the activated sludge chamber itself or in an additional reactor (cross-flow type). These systems effectively remove organic and inorganic compounds as well as biological contaminants from waste water. The efficiency of estrogen removal in membrane bioreactors with nitrification and denitrification is over 90% [20].

The authors did not find significant differences in the removal of EE2 between the two systems and concluded that estrogen removal was mainly caused by biodegradation; the removed estrogens were not absorbed into the sediment particles or retained in the membrane material or membrane biofilm. Weber et al. [21] found that the rotation coefficients E2 to E1 did not differ significantly between conventional and membrane activated sludge. Moreover, no degradation was observed for permanent EE2 in both sediments. While the microfiltration membranes themselves will not provide an increased degree of estrogen removal, it was suggested that the adsorption of estrogens to solid particles retained by the membrane would reduce the concentration of estrogens in sewage. Some researchers found that microfiltration membranes are able to demonstrate some retention of smaller solids or colloidal material on which estrogens can adsorb [22, 23]. Since the pore size of the membrane material is not uniform among manufacturers, it is possible that the difference in membrane material may explain some of the differences in colloidal retention. The differences in detection limits may also play a role.

5. REMOVAL OF STEROID HORMONES WITH BIOLOGICAL NUTRIENT REMOVAL (BNR)

In the biological treatment plants of the BNR, which use biological processes to remove nitrogen and phosphorus compounds, they exhibit significant values for the removal of estrogen. In BNR reactors, for biological removal of phosphorus, an anaerobic zone between the activated sludge and the sewage inflow is necessary, as shown in Figure 5 [24]. Biological removal of nitrogen includes nitrification and denitrification reactions. Nitrification causes the conversion of nitrogen from the reduced form (ammonia) to the oxidized form (nitrate). In BNR reactors the reduction of E1 to E2 takes place under anaerobic conditions, without nitrate. The removal of EE2 takes place largely only under aerobic conditions. According to the studies carried out on E2 and E1

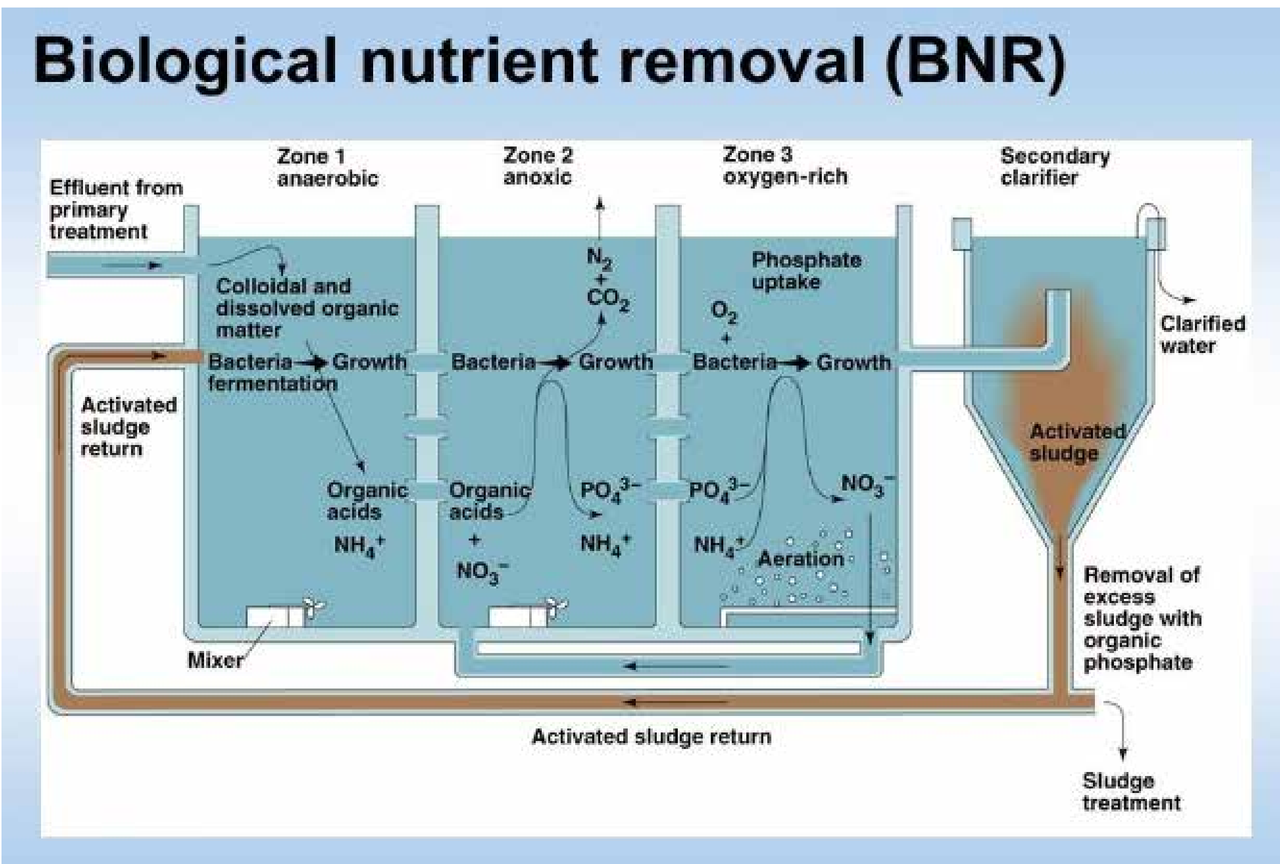


Fig. 5. Biological nutrient removal (BNR) process [24]

decomposition in 18 selected municipal wastewater treatment plants, no statistical correlation was found between HRT or SRT and estrogen removal. Moreover, Josse and others found that the nitrification process showed higher estrogen removal capacity from sewage [25]. Since autotrophic bacteria grow very slowly, a high sediment age is required to achieve nitrification.

The nature of adapted microbiological populations is an important variable in estrogen removal. Servos and others found that the efficiency of E2 removal in municipal wastewater was 80% higher than in industrial wastewater [6]. The system of periodic biotransformation tests using activated sludge showed slight or no transformation of EE2 within 20 hours. However, another laboratory test with nitrifying activated sludge, in which ammonium and hydrazine were the energy sources, showed good results of EE2 removal. Using nitrifying activated sludge (NAS) in the presence of nitrosomonas europaea bacteria oxidizing ammonia, it was observed that NAS degraded 98% of E2 at a concentration of 1 mg/m^3 within 2 hours. The study group also discovered the E1 content when NAS completely removed E2, whereas when Nitrosomonas europaea decomposed E2 compounds, no E1 content was detected either [5]. This suggests that the degradation of E2 by nitrifying activated sludge is caused by other heterotrophic bacteria that exist in NAS and not by nitrifying bacteria such as Nitrodomonas europaea. Heterotrophic bacteria that have been identified in the environment to degrade estrogen include Rhodococcus erythropolis and Mycobacterium fortuitum. Using Rhodococcus strains isolated in activated sludge from a sewage treatment plant, rapid decomposition of highly concentrated ions (100 mg/m^3) of natural and synthetic steroid estrogens (E1, E2, E3 and EE2) was found [26].

6. STEROIDAL ESTROGEN REMOVAL – END OF PIPE MODIFICATIONS

Many of the technologies associated with the water treatment process have been successfully transferred to use in the removal of steroid oestrogen in waste water treatment.

Chemical coagulants such as iron and aluminium salts can be used to remove estrogen from waste water. Schafer and White in their studies presented a comparison of adsorbents used in the water and wastewater industry and found that $FeCl_3$ and MIEX do not show the ability to remove estrogens from wastewater [27]. However, a high removal rate (>90%) can be achieved with powdered activated carbon when added in a sufficiently high dose. Estrogen removal is minimal during coagulation. The researchers found low removal rates (about 18%) for steroid hormones in the sewage treatment plant with chemical precipitation using iron or aluminium salts without biological treatment [27]. Laboratory tests of various doses of ferric chloride and pH conditions showed that coagulation was ineffective in removing E1 from sewage and only a combination of powdered activated carbon (PAC) and microfiltration can be effective in removing estrogens from water and sewage. Moreover, the use of coagulants, such as aluminium and iron salts, is often considered impractical due to high costs and is often environmentally and economically unsustainable [28].

Chlorination has been widely used in the United States as a disinfectant and oxidant for reduced inorganic compounds such as Fe(II), Mn(II) and S(II) in water and wastewater treatment processes. However, disinfection by-products show mutagenic and carcinogenic properties. Studies carried out by Itoh et al. have shown that the chlorination performed in many treatment plants increases the level of estrogen, but also reduces individual strongly estrogenic compounds [29]. Therefore, the authors stressed that the overall effect should be assessed as a sum of increased and decreased chlorination activity. Recent studies have shown that estrogenic activity is usually reduced due to chlorination. Due to EU and river wildlife protection regulations, chlorination is only used to supply drinking water as a disinfectant and not to discharge wastewater.

Membranes can remove most trace micro-pollutants depending on the size of the compound, the chemical conditions of the feed solution and the membrane material. Several studies on oestrogen removal with membranes have concluded that determining the mesh size is very important. Tight and small pore membranes (reverse osmosis (RO) and nanofiltration (NF)) can achieve up to 90% removal, while large pore membranes (microfiltration and ultrafiltration) show less removal [30]. The results of the study to investigate the removal of 52 steroidal estrogens with NF and ultrafiltration (UF) membranes showed that many steroidal estrogens are retained on NF membranes due to both hydrophobic adsorption and size exclusion, whereas the UF membrane usually retains only hydrophobic steroid hormones due to hydrophobic adsorption [30]. Several researchers have pointed out the important role of adsorption in the removal of estrogen by membranes. They found significant concentrations of accumulated estrogen on hydrophobic microfiltration membranes with empty

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fibers. A reduced retention was observed as the amount of ester accumulated on the membrane surface which leads to potential puncture. Since most organic micro-pollutants or steroidal estrogens have a small molecular size, usually in the range of 150 to 500 Daltons, only those compounds that bind to particles or colloidal organic matter will be physically removed during MF and UF. Although the use of membranes seems promising, several factors need to be considered. The RO and NF systems are very expensive and produce a concentrated discard stream that requires further treatment. Moreover, the membranes are susceptible to soiling, which makes the process less efficient and requires regular cleaning [30].

Granular Activated Carbon (GAC), widely used for water and wastewater treatment, has the ability to remove estrogen at different levels. Adsorption depends on the properties of both sorbent and impurity. The dominant mechanism of removing organic micro-pollutants by means of an adsorption system on active carbon is a hydrophobic effect. However, ion exchange interactions can also take place when removing polar dissolved substances. The researchers found that the amount of absorbed E2 was reduced to about one thousandth in river waters and municipal sewage [31].

Ozone (O_3) is effectively used as a disinfectant and oxidant. Ozone can lead to the transformation of steroid hormones through two strong oxidants: molecular O_3 and free hydroxyl radicals (HO^-) [32]. The hydroxyl radical reacts less selectively with organic micro pollutants whereas the more selective ozone reacts with amines, phenols and double bonds in aliphatic compounds. The removal of estrogens depends on their initial concentrations, the coexisting compounds and their reactivity to ozone and OH radicals. OH radicals are more susceptible to absorption by co-existing compounds, which are relatively high in environmental water. Ozone was not particularly effective in oxidation of iodine contrast agents, and combinations of AOP with ozone did not significantly increase the removal rate [32].

Using manganese oxide (MnO_2), 81.7% EE2 was removed. The initial concentration of 15 µg l-1 EE2 was introduced to tap water and filtered through bioreactors filled with MnO_2 granules [33]. The researchers concluded that large amounts of EE2 were removed due to the adsorption capacity of MnO_2 and its catalytic properties. As the MnO_2 reactor was not yet saturated after 40 days of treatment, they concluded that EE2 was also degraded to other compounds. This treatment gives promising results in the removal of similar estrogenic compounds thanks to the MnO_2 self-regeneration cycle [33].

Ironate (Fe (VI)) is often tested as an alternative oxidant in waste water treatment as it can be used as a dual oxidation and coagulation process. Under acidic conditions, the redox potential of ferrous (VI) ions is higher than that of ozone and is capable of oxidation of phenol, amines and alcohols [34]. The determination of a constant second order of oxidation of EE2 and E2 by Fe(VI) at pH close to neutral ranged from 400 to 900 M-1 s-1, which suggests that significant removal of EDC phenols can be achieved [34].

UV lamps are very often used for microbiological disinfection of water and sewage. It has been reported that several endocrine disrupters are susceptible to transformation during UV radiation as they have chromophores, which encourage the adsorption of UV wavelength light [35]. The direct photolysis of two estrogens E1 and E1 in aqueous solutions exposed to UV-disinfection lamp and high-pressure mercury lamp (UV-vis light) was studied. Photolysis of both estrogens causes cracking and oxidation (A) of the benzene ring with the formation of compounds containing carbonyl groups [35].

7. SUMMARY

Estrogens are excreted from the body in large quantities and can enter the aquatic environment in concentrations that are unacceptable and harmful to aquatic and human organisms, so great attention should be paid to their removal using appropriate processes. Biological processes in STW play a key role in the removal of most hormones, biotransformation, biodegradation and adsorption are used for this purpose. The efficiency of these processes depends to a large extent on such parameters as HRT, sediment age, organic charge and redox potential. Diaphragms are very effective in removing estrogen from wastewater, the efficiency is 90%, but it is quite expensive. It can also be seen that the biological methods of wastewater treatment, effectively dealing with estrogen, the activated sludge technology, as well as BNR reactors, have given very good results.

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