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Sorption of endocrine-disrupting compounds (Estrogens) from water: A review

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Abstract

Estrogens are one of the emerging organic substances usually found in water bodies. Natural steroidal hormones such as estrone, estradiol, and estriol and synthetic ones such as 17-α-ethinylestradiol and mestranol a form of endocrine-disrupting compounds are usually found in drinking water, industrial and domestic waste waters. The various sources of estrogens are: animal waste used as fertilizers, birth control pills, humans but mostly women etc. Recent studies have shown that traces of these hormones found in water can indirectly lead to adverse health effects on aquatic and human lives and sometimes in plants. Nanogram/Liter concentration of estrogens can cause a disorder or reproductive problems in aquatic organisms. Researches have shown the effectiveness and efficiency of adsorption in the removal of estrogens from water and is very promising. Several materials can be used as the adsorbent such as activated carbon, zeolites, chitin, chitosan, and low cost agricultural substances among others.

Keywords: Estrogen, sorption, sorbents, sorbate, endocrine-disrupting compounds

1. Introduction

Environmental pollution has been one of the major problems being faced globally. Human activities in several ways led to the deterioration of the environment and pollution in water bodies. Natural steroidal hormones (estrogens) are one of the emerging substances (organics) found in water bodies, which constitute domestic wastewater, water from treatment plants, drinking water, among others [1].

Estrone (E1), 17-β-Estradiol (E2) and Estriol (E3) produced from the ovaries are naturally occurring estrogens known to be of the class of Endocrine-Disrupting Compounds (EDCs) and some synthetic ones such as 17-α-ethinylestradiol (EE2) and Mestranol (MeEE2) found in water [2]. Estrogens are the names attributed to these hormones, but in some literatures estrogen is usually referred to as estradiol (E2) alone. In this review, estrogens connote all these related hormones E1, E2, E3, EE2 and MeEE2. Among them, Estrone is known to be the least abundant. Nevertheless, it is usually produced by naturally menopausal women. Estradiol is considered to be the strongest, and is found to be the most important in a potent reproductive age in females. In addition, it is considered to be the active estrogen and is produced by women that are yet to reach the menopause stage (at reproductive age). Conversely, Estriol is known to be the weakest of estrogens, and it is normally produced during pregnancy in women.

Fukuhara *et al.* acknowledged that there are many sources of steroidal hormones (estrogens) such as animal waste (manure) used as fertilizers, birth control pills, etc., but stated that human (men and women) remain the main source [3]. Natural and synthetically made estrogens are said to be a potent EDCs found in the environment that have adverse effects on both animal and human lives [4]. Though, there are no allowable standard limits set by nationals or organizations (national and international) on the amount of these hormones (estrogens) that is to be released into the environment such as water bodies. Meanwhile, recent studies have shown that traces of these hormones found in water can indirectly lead to adverse health effects (such as: hormone related cancer, reproductive problems, intersex between a particular specie) on aquatic and human lives, sometimes in plants [5]. Concentration of about 1nanogram/Liter (ng/L) or less can cause a disorder or reproductive problems in aquatic organisms [2, 4, 6].

1.1 Estrogens removal from water medium

There are various wastewater treatment plants that are not designed to remove such traces of estrogen substances during treatment as such adsorption is seen as a promising way of treatment of water and wastewater. Traditional processes of treating wastewater such as activated sludge find it very hard to remove estradiol (E2) adequately [3]. Presence of other substances found in surface water and domestic wastewater secondary effluent plants can affect the adsorb ability of some micro pollutant onto the adsorbent (activated carbon) [7, 8]. Microfiltration, coagulation and activated carbon (powdered) adsorption has been assessed for the removal of trace (E1) and the result revealed that activated carbon has high capacity of adsorbing E1 onto it [7], and E2 is also likely to be high.

The properties and characteristics of the material to be used as adsorbent will play a vital role in the adsorption process. These include the chemical composition of the material, the surface charge, pore size, surface area, etc.; and the hydrophobicity of the sorbate is another factor. The physical and chemical characteristics of the sorbents are also playing a role in the adsorbability of the pollutant or contaminant in the water.

Literatures have shown that various materials had been used as sorbents in removing estrogens from water, as is found in Fukuhara *et al.* who used activated carbon to adsorb estrone and 17-βestradiol from water [3]. In addition, Wen *et al.* studied the removal of estrone from water by adsorption on zeolites [9]. Also, Neale *et al.* used ion exchange resin to sorb micropollutant estrone in a water treatment system [10]. Furthermore, Cai *et al.* used reactive and sorptive material in the removal of natural hormones in dairy wastewater [11]. Moreover, Zhang and Zhou study the removal of estrone (E1) and 17b-estradiol (E2) from water through the use of various adsorbents including granular activated carbon (GAC), chitin, chitosan, ion exchange resin and a carbonaceous adsorbent prepared from industrial waste [4].

This study investigates the sources of estrogen (steroidal hormones), concentration in the environment, and its removal from water by various adsorbents. Estrogen is the selected target compound of this study due to its availability in wastewater effluents, drinking water, domestic waste water, in addition to its relatively low removal effectiveness in current treatment plants, and to address its potential danger to the environment [1, 12].

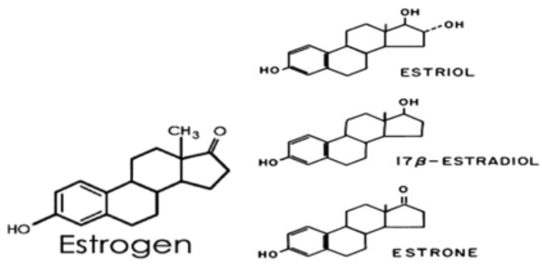

Fig 1: Chemical structure of estrogens

Table 1: Physiochemical properties of Estrogen, E1, E2, and E3

Estrogen	Mol. Wt. (g/mol)	Water solubiity (mg/l, at 0 20 c)	Vapour pressure (mmHg)	Sorption constant (Koc)	Henry's law constant	Log Kow	Structure
Estrone, E1	270.4	13	10 2.3 × 10¯	4882	3.80 × 10 10¯	3.43	C H O 18 22 2
17β estradiol, E2	272.4	13	10 2.3 × 10¯	3300	3.64 × 11 10¯	3.94	C H O 18 24 2
Estriol, E3	288.4	13	15 6.7 ×10¯	1944	1.33 × 12 10¯	2.81	C H O 18 24 3

Source: Silva *et al*. [13].

Fig. 1 shows the chemical structures of various forms of estrogens, and Table 1 summarizes the physiochemical properties of various forms of estrogens stating their solubility in water, molar weight, sorption constant, water partition coefficient (Log Kow) among others.

2. Concentration of estrogen in the environment

Several concentration of estrogen can be found in the environment ranging from wastewater, animal waste, groundwater, and surface water [2]. Johnson *et al*. in their study revealed the excretion of estrogen in females and males per day and divided the females into menstruating, pregnant and menopausal. They further elaborate that females that are menstruating were estimated to excrete about 3.5µg of E2, 8µg of E1, and E3 was about 4.8µg per day from their urine respectively. Similarly, pregnant women were estimated to excrete 259µg of E2, 600µg of E1, and 600µg of E3 per day. Menopausal women were found to excrete about 2.3µg of E2, with 4µg of E1, and 1µg of E3 per day respectively. Males were estimated to excrete 1.6µg of E2 per day, 3.9µg of E1 per day and E3 was put at 1.5µg per day released in their urine. In addition, about 35µg of EE2 was estimated for females that use oral contraceptive pills per day [1].

Sewage treatment plants are also identified to contain some certain amounts of estrogens, both at their influents and effluents in different countries [14, 15]. In sewage treatment plants in Japan, the influents concentration of E2 varies with season: in autumn it ranges from 30-90ng/L, while in summer it was from 20-94ng/L [14]. Similarly, E2 was found in the effluents of Japanese sewage treatment plants, where it ranges from 3.2-55ng/L during summer and from 2.8 to 30ng/L in autumn [16]. Furthermore, the average levels of E1, E2, E3 and EE2 (estrogens) in influents of 6 activated sludge sewage treatment plants in Italy was 52, 12, 80 and 3 ng/L, respectively [15]. In sewage treatment plants of Canada, E1 and E2 were found to have the highest values of 48 and 64ng/L, respectively. In addition, in 9 out of 10 effluent samples measured, EE2 was found to have the highest value of 42ng/L [17]. Highest concentration of 15ng/L for E2, and 2.7ng/L for mestranol in the effluents of sewage treatment plants in South-East Germany was also reported [18].

Meanwhile, several concentrations of estrogens were reported to be found in the environment produced by animal waste through urine. However, steroidal drugs used in cattle and livestock increases the generation of estrogen in them [19]. Cattle treated with muscle building stuffs were found to contain some level of synthetic estrogens in their manure [20]. More so, studies have revealed that application of animal waste (manure) on agricultural land led to the presence of estrogens in surface and ground water due to surface run off and percolation. In the study on karst aquifers in north-west Arkansas, Peterson *et al*. reported a concentration of E2 that ranges from 6 to 66ng/L [21].

3. Sorption process

Sorption is a phenomenon whereby a contaminant (sorbate) gets into and onto the sorbents when treating water. It is applied in the treatment of drinking water, ground water remediation, industrial waste water and domestic waste water for effective use. Isotherm such as Langmuir and Freudlich are mostly used to determine the potential removal capacity of sorbent materials.

3.1 Sorbents used in the treatment of water

Activated carbon (AC) is mostly used in the removal of both natural and synthetic organic compounds (contaminants) from drinking water [22]. Activated carbon can be used in the form of powdered activated carbon (PAC) or granular activated carbon (GAC) [23]. They further stated that AC is suited for the removal of organic compounds due to its pore structure, surface area, functional groups and chemical structure of the substance used. The substances used are coal, palm kernel shell, wood, rice husk, coconut shell and lignin [24]. Both PAC and GAC have enormous potential in adsorbing organic compounds [23]. GAC has demonstrated efficiency in removing estrogen (E1 and E2) from water [3, 4]. Presence of other contaminants in water medium can reduce the efficiency of GAC in its adsorption capability for estrogens [3]. Recent study has shown biologically active carbon filters having greater efficiency than the GAC filters in the removal E2 from water [25]. Zhang and Zhou reported that carbonaceous substances used as adsorbents reached equilibrium faster than the GAC for E1 and E2, E1 reaching equilibrium at 2hours while E2 reached equilibrium at 7hours. However, the study attributed the reason to the smaller pore size and lower concentration of carbonaceous adsorbent (for reaching the equilibrium faster) [4]. Chitin and chitosan are also effective in adsorbing estrogenic compounds, especially chitin been more effective in adsorbing E1 as asserted by Zhang and Zhou in their study. They also reported the kinetics of E1 onto chitin and chitosan that it took a day to reach equilibrium on chitin, and 2 days for chitosan. However, they reported the effectiveness of the following sorbents (carbonaceous substance, granular activated carbon, ion exchange resin, chitin, chitosan) in descending order, as having the capability of removing estrogenic compounds from water [4].

3.2 Sorption of sorbate (estrogens) onto sorbent materials

Snyder *et al*. reported that both GAC and PAC are effective in adsorbing almost all of these compounds (E1, E2, E3 and EE2) as much as above 90% from water medium [26]. In another study, as much as 5-10 µg/L of E3 was adsorbed by activated carbon at a contact time of 180 minute [27]. About 80, 25 and 40% of E1, E2 and E3 were adsorbed respectively by molecular imprinted polymers from water [28]. Meanwhile, a study conducted by Gao *et al*. revealed that carbon nanotubes functionalized by molecular imprinted polymers has high capability of adsorbing E1 (by 96.14 to 98.03%) from water samples [29]. Single-wall carbon nanotubes have the removal efficiency of adsorbing EE2 by about 95 to 98% [30]. However, Kumar and Mohan revealed the potential capability of multi-walled carbon nanotubes to adsorb E2 and EE2, depending on the sorbate concentration and pH in aqueous phase [31].

4. Conclusion

Different studies have shown the danger posed by the accumulation of estrogens in the environment, especially water medium. It has a greater effect on hormone related cancers and reproductive system problems in humans, aquatic organisms, and at large plants. There is need for a more robust study on the minimum concentration that will be harmful to humans as regards to drinking water, and to set a standard for its limit in industrial wastewater and domestic wastewater before being discharged into the environment. More studies should be encouraged on the sorption of estrogens (E1, E2, E3, EE2 and MeEE2) from water so as to cushion the dangers posed, which might be unbearable.

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