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Removal strategies for endocrine disrupting chemicals using cellulose-based materials as adsorbents: A review

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ABSTRACT

Endocrine disrupting chemicals (EDC's) disturb the endocrine system functionality causing negative effects on health in an organism and its progeny. Many studies have reported presence of potential EDC's in wastewater and groundwater, indoor and outdoor air, agricultural soils and food. Epidemiological studies suggest that endocrine disruptors are associated to many worldwide increasing human diseases such as obesity, reproductive abnormalities, cancer, metabolic disorders, cardiovascular risk, autism, and epigenetic alterations.

Effective technological advances for removal of endocrine disruptors in aqueous systems, food matrixes and airborne systems include aeration, ultraviolet irradiation, oxidation, chlorination, coagulation, filtration, biodegradation and membrane technology. However, they still require high investments and operational costs. On the other hand, low-cost cellulose-based materials can be designed for the removal of EDC's via adsorption. Cellulose is the most abundant natural biopolymer, and it can be obtained directly from agricultural wastes, chemically modified and blended with other polymers or manufactured at nano-scale.

This review aims to summarize the most relevant cases where cellulose-based materials have successfully removed EDC's from its environmental matrixes, including technological opportunities foreseen within two categories: native and modified cellulose materials.

Contents

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1. Introduction

Endocrine disrupting chemicals (EDC's) are "exogenous substances or mixtures that alter function(s) of the endocrine system and consequently cause adverse health effects in an intact organism, or its progeny or (sub) populations" [168]. Many of these chemicals are either anthropogenic, e.g. plasticizers, pesticides, pharmaceuticals and detergents [18], or natural, e.g. phytoestrogens and plant secondary metabolites [56]. They reach groundwater after direct discharge, domestic use, accidental spills, and by industrial and agricultural effluents [56]. Consequently, uptake and distribution of endocrine disruptors in many vegetable and fruits crops has been observed indicating a significant potential exposure to humans [104]. It has also been reported the presence of EDC's in processed food, particularly in canned products due to residual bisphenol A (BPA) from can coating that migrates to food product [103]. Furthermore, indoor and outdoor air concentration of potential endocrine disruptors such as PCB's (polychlorinated biphenyls), flame retardants, phthalates, etc. has been reported [144].

Currently, there is a strong debate among regulatory organisms worldwide related to the appreciation of public health dangers associated to endocrine disruptors. For example, EFSA (European Food Safety Authority) Panel deducted that does not exist risks related to BPA dietary exposure but considerable uncertainty in the exposure estimates from non-dietary sources. However, UNEP (United Nations Environment Programme) and WHO (World Health Organization) has emitted its concern on EDC's due to the fact that disorders and diseases of endocrine system are globally on the rise [168]. Furthermore, France has published Law No 2012-1442 for the suspension of the manufacture, import, export and marketing of all-purpose food packaging containing BPA. Nevertheless, a request for the annulment of this law has been filed by the European Association for Plastic Manufacturers and decision still pending [175].

Environmental findings as well as animal and epidemiological studies prompt that exposure to EDC's are associated to obesity [42,127,99], reproductive modifications such as reduced fertility, reproductive tract abnormalities [18], male fish feminization [66], cancer [172,25,95], metabolic diseases, cardiovascular risk [93,123], epigenetic alterations [95,81], autism [46] and other neurobehavioral deficits [22], among others.

Many compounds are suspected to be endocrine disruptors [Table 1], including plasticizers and plastic materials such as di-(2-ethylhexyl) phthalate (DEHP) [111], bisphenol A (BPA) [57,131,117], and styrene [161,13]; persistant organochlorine pesticides and herbicides such as p,p′-dichlorodiphenyldichloroethylene (p,p′-DDE), chlordane compounds [115], dichlorodiphenyltrichloroethane (DDT), 2,4-dichlorophenoxyacetic acid (2,4-D), vinclozolin [119]; pharmaceuticals including paracetamol, aspirin, indomethacin [5,113], ibuprofen [87], synthetic estrogen 17α-ethinyl estradiol [140], natural estrogen 17β-estradiol [163]; compounds present in personal care products such as parabens [26], UV-B filter 4-(methylbenzylidene)-camphor (4-MBC) [35], polycyclic musks fragrances [171]; and dyes [20], for instance methylene blue, acid violet, direct red and Rhodamine B were included on the EPA's list of Universe of Chemicals for Potential Endocrine Disruptor Screening and Testing [55]. Heavy metals like nickel, mercury, cadmium, lead, and uranium are also suspected endocrine disruptors, as well as arsenic [54,61].

Technological advances for EDC's removal include a broad variety of methods, e.g. aeration [14], ultraviolet (UV) irradiation [97], UV/hydrogen peroxide advanced oxidation processes [142], chlorination [128], ozonation [53], reverse osmosis [139], membrane treatment [174], coagulation [116], biodegradation [156,31], sorption [137] and combinations thereof [124,41]. These techniques efficiently remove specific endocrine disrupting chemicals, but still have some limitations such as removal of several EDC's simultaneously, as well as requiring high investments and operational costs. For example, conventional processes of wastewaters treatment have a cost of 1–5 USD/m^3 approximately. In contrast, advanced oxidation processes are estimating to have a cost of a cost of 25 USD/m^3 to remove EDC's such as phenols and tricloroethane [109].

Recently, some reviews regarding the identification, fate, impact and removal of endocrine disruptor chemicals from the environment have been published [32,37,101,28]. These reviews have analyzed conventional techniques such as activated carbon, oxidation, nanofiltration, and coagulation. Two chapter books and a review has focused on the removal of EDC's by adsorption. The two chapter books include thermodynamics background and use of several commercial adsorbents such as activated carbon, clays, minerals, industrial wastes [63,137], as the mentioned review explores the usage of low-cost agricultural sorbents [19].

Adsorption is a very efficient technique for water contaminants removal. Activated carbon has been employed as an effective adsorption material to remove BPA [41]. However, its manufacturing is still a high-cost and complex process that depends on many physicochemical variables such as electrostatic, dispersive and chemical interactions; solute's solubility and ionization constant; pore size distribution; and system's pH and temperature [137].

Cellulose is an alternative raw material for efficient adsorbents production [149] since is the most abundant natural macromolecule on the planet as the main component of plant cell wall. Hemicellulosic agricultural wastes are thus low cost resources and have potential sorption capacities for several pollutants [63]. Remarkably, cellulose can be chemically modified and blended with several natural or synthetic macromolecules for manufacturing tailored materials that remove water pollutants [149,53].

Overall, it is interesting to highlight that it has only been recently studied lipophilic compounds (e.g. atrazine, BPA, ethinyl estradiol, among others) using cellulose-based adsorbents from agricultural wastes. Removal of these compounds it is more likely to have a major impact on human health since living organism's detoxification process depends on the activity of their enzymatic system which converts EDC's into more water soluble forms to be excreted via urine [177]. Lipophilic compounds tend to accumulate in the brain, breast milk and cell membranes causing neurobehavioral disorders and other epigenetic alterations [22].

The present review aims to summarize recent advances related to cellulose-based materials as a rising technology for endocrine disruptors removal from environmental matrixes. It is included adsorption properties of cellulose-based materials and list technological opportunities foreseen within two categories: native and modified cellulose materials. It is our hope that this paper helps to inspire more research on the design of cellulose-based materials as adsorbents to remove EDC's.

2. Adsorption properties of cellulose

Cellulose is integrated by units of β-D-glucopyranose linked by (1 → 4) glycosidic bounds. The pyranose rings are in a chair conformation with equatorial and axial hydroxyl groups. The degree of polymerization (DP) range from 100 to 20 000 glucopyranose units. Cellulose hydroxyl groups generate hydrogen bonds within the sheets and inter-molecularly van der Waals forces, so the crystalline structure is created [129,65]. In plants, native cellulose involves three crystalline allomorphs: cellulose Iα, cellulose Iβ and *para*-crystalline cellulose, as well as two non-crystalline forms: amorphous at fibril-water contact surfaces and fibril-fibril contact surfaces [70].