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Review

Typical low cost biosorbents for adsorptive removal of specific organic pollutants from water

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HIGHLIGHTS

- Characteristics of lignocellulosic sorbents and chitin/chitosan were analyzed.
- Uptake mechanism of SOPs was revealed and discussed.
- Modification methods to enhance biosorbents were presented.
- Application of typical low-cost biosorbents to remove SOPs was assessed.
- Future viewpoint to use inexpensive biomaterials for SOPs elimination was proposed.

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ABSTRACT

Specific organic pollutants (SOPs) such as phenolic compounds, PAHs, organic pesticides, and organic herbicides cause health and environmental problems due to their excessive toxic properties and poor biodegradability. Low-cost biosorbents are considered as a promising alternative for conventional adsorbents to remove SOPs from water. These materials have several advantages such as high sorption capacities, good modifiability and recoverability, insensitivity to toxic substances, simple operation in the treatment processes. However, previous reports on various types of biosorbents for removing SOPs are still moderately fragmented. Hence, this paper provides a comprehensive review on using typical low-cost biosorbents obtained from lignocellulose and chitin/chitosan for SOPs adsorption. Especially, their characteristics, biosorption mechanism together with utilization for eliminating SOPs are presented and discussed. The paper also gives a critical view regarding future applications of low-cost biosorbents in SOPs-contaminated water treatment.

1. Introduction

Organic pollutants have become an increasing concern due to their potential of mutagenicity, carcinogenicity, teratogenicity and high bioaccumulation (Abdeen and Mohammad, 2013; Chen et al., 2011; Valili et al., 2013). The adverse effects on health and the environment caused by specific organic pollutants (SOPs) such as phenolic compounds, polycyclic aromatic hydrocarbons (PAHs) and agricultural chemicals (organic pesticides and organic herbicides) have been considered as critical problems (Chen et al., 2011; Ahmed and Mohammad, 2014; Nanseu-Njiki et al., 2010; Nagda et al., 2007). World Health Organization has established a very strict legislation for these compounds in WHO (2011) Guideline for Drinking-Water Quality (Fourth Edition). For example, the limits of 2,4,6 trichlorophenols (phenolic compound), benzo(a) pyrene (PAH), dichlorodiphenyltrichloroethane and metabolites (pesticide), and 2,4-dichlorophenoxyacetic acid (herbicide) were set at 200×10^{-3}, 0.7×10^{-3}, 1×10^{-3}, and 30×10^{-3} mg/L, respectively. As a consequence, abatement of these compounds from water is indispensable for protecting human health and the environment.

Several available techniques (e.g. photocatalytic degradation, combined photo-fenton and ultrasound, advanced oxidation, aerobic degradation, filtration, ozonation, coagulation, flocculation, distillation, extraction, precipitation, and adsorption, etc.) have

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been developed for SOPs removal from water (Ahmad et al., 2010; Ahmed and Mohammad, 2014; Al-Zaben and Mekhamer, 2013; Kong et al., 2012; Pal, 2012; Pham et al., 2012). Among them, adsorption has superior advantages over other methods for removing pollutants at low concentration with respect to environmental friendliness, economy and high efficiency (Chen et al., 2011; Xi and Chen, 2014; Yakout and Daifullah, 2013). Nevertheless, the expensive manufacturing cost makes conventional adsorbents such as activated carbon less economically feasible for extensive use in water treatment (Ata et al., 2012). The use of non-conventional, low-cost biosorbents prepared from agricultural wastes and by-products can not only reduce a large quantity of solid waste but also be very attractive. Their benefits are mentioned, including low investment cost, simplicity of design and operation, insensitivity to toxicants and a remarkable performance even with very low concentration solutions (Mohammad, 2013). It was reported that biosorption could reduce 20%, 36% and 28% of capital, operational and total cost in comparison with conventional systems, respectively (Ata et al., 2012).

The uptake capacity and stability of biomaterials can be enhanced by physical and chemical modifications with heat (drying and pyrolysis), de-sugared, and inorganic/organic activants (e.g. H_3PO_4, HNO_3, HCl, H_2SO_4, NaOH, $KMnO_4$, CH_3OH, methacrylic, methanol, acetone, etc.) (Abdeen and Mohammad, 2013; Akhtar et al., 2006; Li et al., 2009; Nagda et al., 2007; Xi and Chen, 2014; Yakout and Daifullah, 2013). In addition, tons of cheap biosorbents belonging to some principal categories (including lignocellulose, algae, chitin/chitosan, activated sludge, bacteria biomass, fungal biomass, and so on) are able to be used for SOPs removal (Aksu, 2005; Abdolali et al., 2014; Ahmad et al., 2010). Among these categories, lignocellulose and chitin/chitosan are great applicable groups because of their representativeness, high adsorption capacity and availability. In terms of sorption capacity, it is determined by either the presence of lignin and silica in lignocellulose structure, or the rich contents of amino and hydroxyl functional groups in chitosan or chitin's derivative (Xi and Chen, 2014; Abdeen and Mohammad, 2013).

Although applications of biosorbents on treating heavy metals have been extensively examined (Abdolali et al., 2014; Nguyen et al., 2013; Hossain et al., 2012), studies on removing SOPs were only emerging in recent years (Ahmad et al., 2010; Bhatnagar and Sillanpää, 2009; Srivastava et al., 2009; Zolgharnein et al., 2011). Research on this issue mostly focused on single groups of SOPs on different types of adsorbents. For instance, papers on pesticide removal from water by different materials including conventional and low-cost biosorbents mainly focused on adsorption capacities as well as experimental conditions (Ahmad et al., 2010; Srivastava et al., 2009; Zolgharnein et al., 2011). There is a lack of reviews discussing relationship between characterization of biosorbents and mechanism as well as adsorption capacities for all four kinds of SOPs (phenols, PAHs, pesticides and herbicides).

To demonstrate the feasibility of using low-cost biosorbents prepared from lignocellulose and chitin/chitosan for SOPs removal, this paper presents a comprehensive review with focused discussions on five key sections: (i) characteristics, (ii) biosorption mechanisms, (iii) maximum adsorption capacities, (iv) methods to produce better biosorbents and (v) utilization of biosorbents for SOPs removal.

2. Characteristics of typical biosorbents

Physical and chemical characteristics of biosorbents are very important to understand adsorption mechanism as well as potential application of the materials. Therefore, this section discusses the characterization of typical low-cost materials from lignocellulose and chitin/chitosan. Table 1 summarizes the characteristics of biosorbents which determined their adsorption process for SOPs from water.

2.1. Lignocellulose

Key characteristics for determining SOPs adsorption on lignocellulosic materials include chemical composition, functional groups, surface area, porosity and surface morphology.

The most significant characteristic of lignocellulose affecting its adsorption behavior is chemical composition. As the primary building block of plant cell walls, lignocellulose contains cellulose, hemicellulose, lignin and a little amount of pectin, protein, vitamins, lipids, extractives, combined with ash (Jørgensen et al., 2007). Chemical compositions of lignocellulose can be characterized by X-ray Photoelectron Spectroscopy, X-ray Diffraction, and chemical analysis. The chemical compositions of some typical low-cost lignocellulosic adsorbents are shown in Fig. 1 (Ferraz et al., 2000; Ismail et al., 2002; Khalil et al., 2007; Khiari et al., 2010; Krishnani et al., 2008). Plants residues such as wooden materials, coconut shell, pineapple leaves, banana stem, sugar cane bagasse, coffee waste have the highest cellulose contents (>40%). The highest lignin content (>30%) appears in biomass like neptune grass, soft wood, coconut shell and bark. According to Xi and Chen (2014), adsorption capacities of biosorbents could be affected by some factors such as polarity and aromaticity. In which lignin is assumed to be the main storage medium of organic pollutants and higher lignin content results in higher affinity with persistent organic pollutants. The authors further pointed out that the adsorption potential of lignin was seriously restricted by polar components. This hypothesis suggested that low sugar content (polar component) could enhance adsorption ability of pine needles for persistent organic pollutants (Chen et al., 2011). In addition, ash content of lignocellulose also played an important role in the adsorption process of organic pollutants on these materials. The ionic structure of silica ($SiO_4{\cdot}4H_2O$) in ash content provides a capability of adsorbing polar molecules as phenols (Akhtar et al., 2006).

Another important factor for binding SOPs on lignocellulose is the existence of functional groups such as hydroxyl (–OH), carboxyl (–COOH) and silanol (Si-OH), which are responsible for sorption of organic pollutants from the aquatic environment (Akhtar et al., 2006; Aksu, 2005; Krishnani et al., 2008; Abdolali et al., 2014). According to Mohammad (2013), functional groups are responsible for pesticides removal by lignocellulosic materials. Olivella et al. (2013) also proposed mechanisms of phenanthrene sorption by cork relating to aromatic rings of lignin and carboxyl groups ($-COO^-$) in the biosorbent. Functional groups of lignocellulosic materials were often qualitatively determined by Fourier Transform Infrared Spectroscopy (FTIR). Xi and Chen (2014) employed FTIR technique to explore sorption mechanism of PAHs on several raw and modified plant residues and found that aromatic bands were major functional groups in de-sugared materials which has better adsorption capacities than raw biomass. The authors concluded that the de-sugared or hydrolyzed biomasses are promising biosorbents for removing PAHs. From FTIR analysis, Ahmed and Mohammad (2014) reported that some surface functional groups such as –OH, alkyne, aromatic rings, ketone, aldehydes, lactones and carboxyl might be involved in the pesticide removal on apricot stone activated carbon.

The surface area and porosity of lignocellulose that were analyzed by Brunauer–Emmett–Teller (BET) method also greatly affect their SOPs adsorption capacities. The International Union of Pure and Applied Chemistry (IUPAC) recommended classification of materials based on their total porosity. Accordingly, adsorbents can be divided into three categories, namely macropores ($d > 50$ nm), mesopores ($2 < d < 50$ nm) and micropores ($d < 2$ nm). In raw form, the surface areas of plant residues are quite small,