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Chitosan-based biosorbents: Modification and application for biosorption of heavy metals and radionuclides

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HIGHLIGHTS

- Chitosan can be easily modified by versatile methods.
- The preparation and modifications of chitosan were introduced.
- The application of chitosan-based sorbents for heavy metal removal was presented.
- Chitosan-based biosorbents are potential for biosorption of heavy metals.

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ABSTRACT

Heavy metal pollution is a serious environmental problem in the world, especially in developing countries. Among different treatment technologies, biosorption seems a promising alternative method. Chitosan-based biosorbents are potential and effective for heavy metal removal from aqueous solution. The preparation and characterization of the natural polymer chitosan, modified chitosan and chitosan composites, and their application for the removal or recovery of toxic heavy metals, precious metals and radionuclides from wastewater were introduced. Chitosan structures and their properties, chitosan modifications (physical conditioning and chemical modification), blends and composites as well as the metal sorption by chitosan-based biosorbents were briefly presented. The metal sorption capacities, influence of intrinsic nature of metal ions, pH and contact time, desorbing agents, isotherm and kinetics models, biosorption mechanisms were discussed.

1. Introduction

1.1. Heavy metal and radionuclide pollution

Heavy metal pollution is becoming a serious threat to ecosystem and human health through polluting water, soil and air in some parts of the world. The most important heavy metals include lead (Pb), mercury (Hg) and cadmium (Cd), which are considered to have dangerous environmental impacts according to their toxicological criteria (Volesky and Holan, 1995). Chromium (Cr), arsenic (As) or selenium (Se) are also toxic. In fact, lead (Pb), mercury (Hg), cadmium (Cd), chromium (Cr) and arsenic (As) are commonly considered as the priority heavy metals due to their high toxicity, prevalent, existence and persistence in the environment. Nickel (Ni) and vanadium (V) are widely used. The common metals, zinc (Zn) and copper (Cu), are essential elements for various life, but they are also toxic when in high concentration. Precious metals or noble metals such as gold (Au), silver (Ag), palladium (Pd), and platinum (Pt) always attract much attention mainly in order to concentrate and effectively recover from dilute solutions, even if they would not pose environmental threats. Some heavy metal occur as anions, such as hexavalent chromium (Cr(VI)), molybdenum (Mo(VI)), trivalent gold (Au(III)), Se(V), vanadium (V(V)) and arsenic (As(V)) with different properties from those of the usual metal cations. Radionuclide is the third important category metal in terms of environmental impact and interest from nuclear industry, such as nuclear facilities, nuclear power plant or nuclear weapon testing. Uranium (U), thorium (Th), radium (Ra), polonium (Po), strontium (Sr-90), cesium (Cs-137) or cobalt (Co-60) are of importance for its environmental impact and human health effect (Volesky and Holan, 1995). The half life of these isotopes is a very important parameter to decide the hazardous level of the radionuclides. Uranium is an important nuclear fuel resource as well as one of main radioactive

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elements in the radioactive liquid wastes, although naturally occurring uranium is not particularly a problem in the environment. Radium-226 (Ra-226) is the most hazardous isotope found in the tailings, and it is very important. Thorium (Th) is used in variety of industrial purposes, medical applications and proposed as fissile material for nuclear energy via production of U-233 from Th-232 (Volesky and Holan, 1995). Long-lived radionuclides of Cs-137 (half life of 30.17 years), Sr-90 (half life of 28 years) and Co-60 (half life of 5.27 years) are considered as the most dangerous to human health due to their high transferability, high solubility, long half-lives and easy assimilation in living organisms among the fission by-products. Due to its chemical similarity with potassium (K) for Cs or calcium for Sr, Cs-137 and Sr-90 can easily transfer and reach the human body, exerting persistent radiological impact to environment and human body.

Physical, chemical and biological methods for metal removal or recovery from wastewater have been extensively researched and/or applied, such as chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation and flocculation, flotation, electrochemical methods (Fu and Wang, 2011). Treatment technologies of heavy metal contaminating wastewater can be classified into three types: (1) by chemical reaction for metal removal, such as chemical precipitation, chemical reduction and electrolysis. (2) by sorption, enrichment, separation processes for metal removal without alteration of metal state, e.g. active carbon adsorption, extraction, ion exchange, reverse osmosis, electro dialysis, evaporation, etc. (3) by biological process with adsorption, accumulation and enrichment mechanisms for metal removal, e.g. biosorption, bioflocculation, constructed wetlands, etc. The complicated wastewater requires the integrated technologies for wastewater treatment for toxic heavy metals, precious metals, radionuclides. To meet the stricter environmental standard, to protect environment and to save resources, development of viable and diversity in relevant technologies that can not only clean-up but also recover valuable components from industrial waste streams is of utmost importance.

1.2. Chitosan-based biosorbents

Among those mentioned methods, adsorption/biosorption process is one of the effective methods to remove heavy metals from water and wastewater (Crini, 2005). Numerous studies have been carried out to create various suitable or new sorbents/adsorbents/biosorbents for heavy metal removal from aqueous solution (Guibal, 2004; Gerente et al., 2007; Crini and Badot, 2008; Fu and Wang, 2011). Chitin is abundant naturally occurring basic polysaccharide, mainly from animals, existing in crustacean shells such as shrimps, prawns, crabs and lobsters, in insects such as beetles, in cuttlefish of bone, in fungi such as mushrooms (Uragami and Tokura, 2006). Chitin is a linear polysaccharide with β-1,4 bonded 2-acetoamide-2-deoxy-D-glucose (N-acetyl-D-glucosamine). Chitosan is the deacetylated form of chitin. With the advantages of the widespread abundance, high safety, low toxicity, good chemical reactivity, chemical and physical versatilities, chitin and chitosan characteristics have lead to the studies and developments in widespread applications, such as in biomedical and environmental field. Chitin and chitosan are of commercial interest for their high percentage of nitrogen (6.89%) compared to synthetically substituted cellulose (1.25%) (Kumar, 2000). Both chitin and chitosan have numerous application in many fields, including biomedical, pharmaceutical, microbiological, food preservatives, environmental protection and so on.

Chitosan and chitin were mainly used for removing pollutants through coagulation (4%), precipitation (7%), flocculation (3%), adsorption (28%), flotation (1%), filtration (4%), membranes filtration (53%) (Crini and Badot, 2008). Chitosan with high content of amino and hydroxyl groups can be used as sorbents for purification of wastewater containing heavy metals, radionuclides and dyes (Gerente et al., 2007; Crini and Badot, 2008; Chen and Wang, 2012c; Liu et al., 2013; Yong et al., 2013). Many researchers are endeavoring to develop various chitosan-based materials for metal removal (Guibal et al., 1998; Guibal, 2004; Varma et al., 2004; Gerente et al., 2007). Due to the nature of chitin and chitosan as natural polymers, the term of "sorbents" (Guibal, 2004), "adsorbents" (Yong et al., 2013) or "biosorbents" (Guibal, 2004; Crini and Badot, 2008) has been used. Accordingly, the term of "sorption", "adsorption" or "biosorption" without clear and specific differentiation occurred in some published references to describe the metal removal process by the chitin/chitosan-based materials.

Several review articles on chitosan-based biosorbents, much or less related to heavy metal removal have been published, including using chitosan and its derivatives as biosorbents for metal removal, modifying chitosan derivatives (Wu et al., 2010), investigating on the interaction of chitosan with heavy metals (Guibal, 2004; Muzzarelli, 2011), investigating the various factors, modifications, operation modes, sorption behavior modeling on metal sorption (Crini, 2005; Guibal, 2004; Varma et al., 2004; Gerente et al., 2007; Crini and Badot, 2008; Ngah et al., 2011), metal sorption (such as Hg) (Miretzky and Cirelli 2009), for heavy metal and dye removal (Ngah et al., 2011; Liu et al., 2013), Sulfur-containing chitosan-based biosorbents for metal removal (Yong et al., 2013), development of chitin and chitosan (Pillai et al., 2009), chitin and chitosan modification (Kurita, 2001; Mourya and Inamdar, 2008) and their potential biomedical, environmental or other applications (Kumar, 2000; Rinaudo, 2006; Jayakumar et al., 2005; Bhatnagar and Sillanpaa, 2009; Liu et al., 2013; Yong et al., 2013).

Guibal (2004) gave an excellent review on the interactions between metal ions and chitosan-based sorbents, not only for the decontamination of effluents, for the recovery of valuable metals but also for the development of new materials or new processes involving metal-loaded chitosan. Varma et al. (2004) reviewed on chitosan-based biosorbents–metal interactions, according to the classification of the modified chitosan and its derivatives like crosslinked chitosans, templated chitosans, derivatives of chitosan containing N, P and S as heteroatom, other derivatives of chitosan (chitosan crown ethers, chitosan EDTA/DTPA complexes, chitosan graft copolymers, chitosan graft sugars, chitosan derivatives with 1,3 dicarbonyl compounds, chitosan–cyclodextrin conjugates, halogenated derivatives). Bhatnagar and Sillanpaa (2009) summarized the principal results of application chitin and chitosan-derivatives for removing metals (cations and anions) and radionuclides, dyes, phenols and other miscellaneous pollutants. Miretzky and Cirelli (2009) reported Hg(II) removal from wastewater using chitosan and its derivatives. Wu et al. (2010) analyzed the sorption capabilities of pristine and modified CTS for heavy metals (such as Cu (II), Zn (II), Ni (II), Cd (II), Pb (II), Hg (II), and Cr (VI) from aqueous media according to the Langmuir equation based on their experimental data. Ngah et al. (2011) introduced various chitosan composites for adsorption of dyes and heavy metals, including chitosan/ceramic alumina composites, chitosan/oil palm ash composites, chitosan/magnetite composites, chitosan/cotton fiber composites, chitosan/sand composites, chitosan/cellulose composites, chitosan/montmorillonite composites, chitosan/polyvinyl alcohol (PVA) composites, chitosan/polyvinyl chloride (PVC) composites, chitosan/calcium alginate composites, chitosan/bentonite composites. Gerente et al. (2007) provided the detailed model analysis on metal removal by chitosan, including various equilibrium isotherms, various kinetic models. Muzzarelli (2011) briefly presented an interdisciplinary review with comprehensive and deep insight in interactions of chitosan with heavy metals including