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Review

Versatile nature of hetero-chitosan based derivatives as biodegradable adsorbent for heavy metal ions; a review

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ABSTRACT

The polyfunctional chitosan can act as the biological macromolecule ligand not only for the adsorption and the recovery of metal ions from an aqueous media, but also for the fabrication of novel adsorbents which shows selectivity and better adsorption properties. The unmodified chitosan itself, a single cationic polysaccharide, has hydroxyl and amine groups carrying complex properties with the metal ions. In addition, the selectivity of metal ions, the adsorption efficiency and adsorption capacity of the adsorbent can be modified chemically. This review covers the synthetic strategies of chitosan towards the synthesis of hetero-chitosan based adsorbents via chemical modifications in past two decades. It also includes how chemical modification influences the metal adsorption with N, O, S and P containing chitosan derivatives. Hope this review article provides an opportunity for researchers in the future to explore the potential of chitosan as an adsorbent for removal of metal ions from wastewater.

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1. Introduction

Growing industrialization from last ten years has been the cause of pollution and reduced water quality. This is a big issue in developing as well as developed countries [1]. The waste material exposed from industries is discharged into water bodies, carrying heavy metals which produce a lethal effect on the biological life in aqueous systems. Biological life on earth without aqueous media is impossible; hence it is of great importance to remove the heavy metals from the wastewater. Industrial wastewater is comprised of various metal ions such as arsenic, mercury, lead, copper, chromium, nickel, cobalt, etc. Some of these metals have toxic effects even at low concentration due to their toxic nature such as mercury. The funda-

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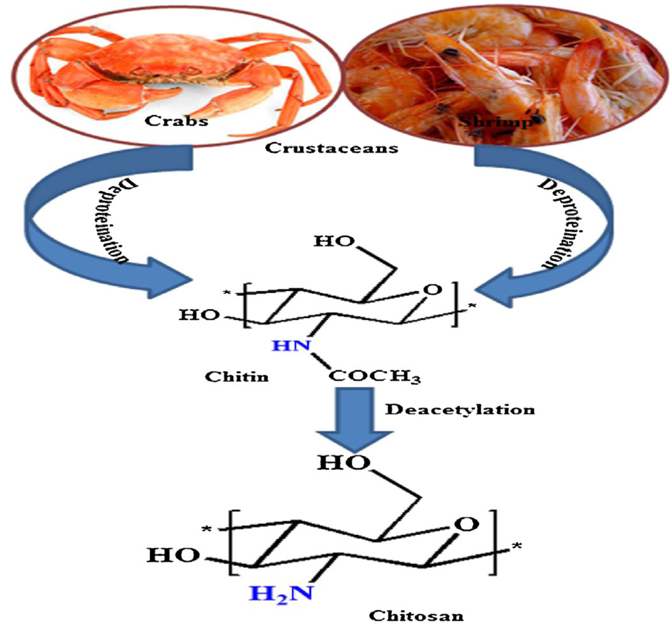
mental sources of mercury emission are natural, anthropogenic and re-emission [2]. Exposure to mercury leads to its increasing concentration in blood, resulting in its accumulation in organs causing diseases such as neurological disorder and damage to cardiovascular, kidney, and bone tissue [3–5]. In global environment, arsenic exists in two forms as arsenate and arsenite. The latter is 25–60 times more toxic and mobile than the former [6]. It is observed that arsenic has lethal effects on biological life. Arsenic exposure causes cancer in the lungs, skin, urinary bladder and kidneys [7]. It can also change the thickness of the skin. Short exposure of arsenic can cause vomiting, along with abdominal and esophageal pain [8]. Among of all the heavy metals copper is most common contaminant released in wastewater. The common sources of copper are metal cleaning and plating, textiles and paper mills, and wood and pulp industries [9]. Copper exposure occurs through food, water and dust. In certain cases, it may accumulate in the liver, which causes gastrointestinal disorders and long term exposure causes liver and kidney damage [10]. The hereditary diseases such as Wilson disease, is caused due to copper accumulation in liver, brain and other tissues which in turn leads to dysfunction of these tissues, eventually leading to death [11]. On the other hand, at low concentrations copper is an essential nutrient for biological life but its slight rise in concentration is harmful for cellular activities [12]. Although, removal of these toxic metal ions is not easy, there are various techniques used for metal removal from the wastewater, such as ion exchange, chemical precipitation, membrane filtration, electrochemical methods and adsorption [13]. Among all these, adsorption is the most convenient technique, due to its attractive adsorption efficiency, low cost and easy handling. One more important feature is the regeneration and recovery of the adsorbent and metal ion respectively [14]. Biopolymer based adsorbents such as chitosan, cellulose, alginate, lignin etc., play an important role in the adsorption due to their biocompatibility and reabsorbability [15]. Among these chitosan plays a significant role towards the adsorption process, due to its hydroxyl and amino groups which participate in the metal adsorption process. Chitosan a polyaminosaccharide, obtained from chitin, by deacetylation process shown in Scheme 1, “the second most common” biopolymer after cellulose [16]. It consists of mostly unbranched chains β-(1 → 4)-2-acetoamido-2-deoxy-D-glucose. However, one major limitation of chitosan is that it is insoluble in aqueous solution but soluble in acidic media (dissolve $pH \geq 4$) [17,18]. The researchers made various efforts to overcome the acidic resistance of chitosan through chemical crosslinking of the surfaces with crosslinking agents such as, ethylene glycol diglycidyl ether [19], glutaraldehyde and epichlorohydrin [20]. Chemical crosslinking indeed minimizes the solubility of the chitosan matrix at low pH. However, the crosslinking reagents are prone to combine with the amine groups instead of hydroxyl groups of the chitosan matrix. These amine groups are the main reagents that take part in adsorption [21]. Hence, crosslinking reduces the adsorption efficiency of the chitosan. To preserve its adsorption efficiency numerous methods are applicable that can prevent the amino groups from crosslinking. New crosslinking regents are used to shield the amine groups and subsequent release of amine groups for adsorption of metal ions [22]. Various researchers are interest in the syntheses of chitosan based adsorbents, which are ecofriendly, cost economic and have high adsorption efficiencies. Li et al. synthesized thiosemicarbazide chitosan for the adsorption of Pb(II) and Cd(II) ions from wastewater [23]. The adsorption efficiency is more due to the presence of chelating groups, the addition of thiosemicarbazide not only stabilizes the chitosan in acidic medium but also makes it capable of the chelation of selective metals such as Cu(II) and Hg(II) [24]. Chitosan derivatives have been extensively used for the adsorption of heavy metal ions [25], containing heteroatoms such as N, O, S, P, and other chitosan crown ethers, such as chitosan diethylenetriaminepentaacetic acid/ethylenediaminetetraacetic acid complexes [26]. Recently chitosan composites have been synthesized through modification for adsorption of selective metal ions. Various substances, such as polyurethane [27], activated clay [28], bentonite [29], kaolinite and polyvinyl alcohol [30] have the carrying ability to prepare composites with chitosan. This review paper highlights the adsorption of metal ions via chitosan based adsorbents, synthesis, application, mechanism and the factors that influence the adsorption efficiency as well as adsorption capacity. We hope this article assists researchers in future to design novel types of chitosan based adsorbents which carry better adsorption capacity and higher efficiency to resist low pH in aqueous media.



Scheme 1. Shows the extraction process and structure of chitin and chitosan.

2. Physical and chemical properties of chitosan

Chitosan is an important biopolymeric waste product produced from crustaceans. Chitin is mostly produced from the crab shells; it also contains proteins, caroteins and calcium carbonate. Prawn, crab and lobster are main sources of chitin contributing almost 15–20% [31]. It is a polysaccharide similar to cellulose structure with β-(1 → 4)-2 acetamido-2-deoxy-D-glucose units. The structure of chitin is shown in Scheme 1. Chitosan is a partially deacetylated polymer obtained from chitin. It is polyaminosaccharide with glucose like structures connected with poly (1 → 4)-2 amino-2-deoxy-D-glucose units, as the structure is shown in Scheme 1. Chitin is found in wide range of natural organisms like, insects, crustaceans, molluscs, coelenterates. However, chitosan is obtained only from a few such as crustaceans (crab, crayfish), of which several million tons are obtained annually, a large amount of this about 50% is discarded as a shell waste. The molecular mass of chitosan depends on the processing as commercial development of the product. The different grades of chitosan range from 10,000 to 1,000,000 Da, and are available from different manufacturing companies with different degree of deacetylation. It usually ranges from 70 to 90%. Degree of deacetylation means mole fraction of deacetylated units present in the polymer backbone [32].