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Review Article

Synthesis and characterization of molecular imprinted nanomaterials for the removal of heavy metals from water

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ABSTRACT

Heavy metal pollution presents an important global environmental problem due to its toxic effects that may accumulate in the food chain. For removal of toxic heavy metals from different sources of water, various technologies such as chemical precipitation, membrane filtration, solvent extraction, electrodialysis, ion exchange and adsorption are employed. However, only the adsorption method is the most versatile and widely used, while others are more expensive and of low feasibility. A wide variety of porous materials, such as agricultural waste, polymers, clay minerals and carbon materials have been investigated as adsorbents for the removal of toxic metals. In this study, the adsorbent stability in acidic and basic medium, desorption study as well as its reusability and recyclability were adequately assessed. The effect of contact time, pH and adsorbent dose were addressed by various authors, which specifies the reliability and efficiency of nanoparticles as potential adsorbents. The molecular imprinted (MI) nanomaterials are also suitable for a broad spectrum of applications such as biosensing, molecular imaging, and drug delivery. However, there are certain setbacks that can be reduced or diminished through the coating of nanoparticles with various polymers of biological origin. These biopolymers are biocompatible, non-toxic and renewable. They possess chemical groups that permit further functionalization of the MI nanoparticles. Multifunctional entities can be created through decoration with specific molecules e.g. proteins, peptides, drugs, antibodies, cells and transfection agents. Therefore, MI nanomaterials may be used as the future materials for the environment and human sustainability.

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1. Introduction

Water pollution is one of the most serious problems that have been addressed by several water pollution controlling bodies at national and international levels. Water contaminated with toxic metals is considered as a serious environmental problem in human society [1]. Heavy metals in water originate from geological erosion and natural calamities as well as rapid development of human civilization, such as industrialization, urbanization, mining operation, atomic power plants, pharmaceuticals, pesticides, forest fire and tanneries [2]. Heavy metals are elements having atomic weights between 63.55 and 200.59 and a specific gravity greater than 4.0. Living organisms require trace amounts of some heavy metals including Co, Cu, Fe, Mn, Mo, V, Sr, and Zn. They are known as essential metals but their excessive levels can be detrimental to organisms. Heavy metals including Hg, Cr, Cd, As, Pb, Sr, etc. are nonessential metals and considered to be a great threat to aquatic life as well as humans, plants, and other living beings [3]. These heavy metal ions are directly released into the natural water by various industrial and human activities. These metals exist in surface water in colloidal, particulate and dissolved forms, although dissolved concentration is very low and are generally in the form of ions or unionized organometallic chelates or complexes. The solubility of trace metals in surface water is controlled by the water pH and the type of concentration of ligands on which the metal could adsorb such as clay, silica, alumina and organic matter [4–6]. The colloidal and particulate forms of metals are found in hydroxides, oxides, silicates, sulfides that get adsorbed to clay, silica and organic matter. These toxic metals are not only threat to the aquatic organisms but also cause severe health disorders in humans by accumulation through food chain [7]. The toxicity of heavy metals may be caused by the inhibition and reduction of various enzymes, complexation with certain ligands of amino acids and substitution of essential metal ions from enzymes [8].

Nowadays small and large scale industries are discharging their effluents directly into the water sources and thus polluting them with toxic metals. Toxicological studies have found that the degree of toxicity of heavy metals depends on the oxidation state of metal ions [9]. For instance, chromium is a common contaminant in industrial effluent water of electroplating, tanning, paint and pigment production as well as metallurgical industries. It is usually presented in the environment in two stable oxidation states Cr(III) and Cr(VI). It is well known that chromium(III) is considered as an essential micronutrient for human, plant and animal metabolism, while chromium(VI) is soluble and hazardous to health. In natural water chromium ions mainly appear as chromate and cationic hydroxo complexes. The recommended limits for Cr(VI) in drinking water is 0.05 ppm [10]. Copper(II) play a crucial role in the development of bones, central nervous system, and connective tissues. The acceptable limit of Cu in drinking water is 2.0 mg/l [11], but its concentration varies from 0.01 to 0.5 mg/l, which is tolerable and poses no serious health threat to the human and living organism [12]. Cadmium(II) is highly toxic and cause a number of acute and chronic disorders, such as renal damage, emphysema, hypertension and skeletal malformation in the fetus [13–15]. The maximum concentration of Cd in potable water is 0.005 mg/l [16,17]. Arsenic is presented in two forms: organic and inorganic. Inorganic arsenic is a commonly known carcinogen [18]. The maximum acceptable concentration of As in drinking water is 0.01 mg/l [19]. Mercury that deposits onto the earth's surface from the air can make its way into waterways, where it is converted by microorganisms into the organic compound dimethyl mercury, a highly toxic form of mercury, which has been implicated in causing brain and liver damage [20]. Methyl mercury concentrations increase with food chain levels, i.e., bioaccumulation [21–23]. As a result, consumption of food (mercury-contaminated fish) by humans (pregnant women) causes developmental effects in their offspring such as low intelligence levels, delayed neurodevelopment and subtle changes in vision, memory and language [24]. The maximum acceptable concentration of Hg in drinking water is 0.001 mg/l [25,26]. Lead can enter the human body through water, food and air. Its implication can be seen in the form of kidney damage, miscarriage, brain damage impulsive behavior and hyperactivity. Long-term exposure to lead or its oxides can cause nephropathy [27]. Its concentration in drinking water is 0.01 mg/l [28]. Hence, removal of heavy metals from wastewater and drinking water is of great importance due to their serious health effects [29]. Various technologies such as chemical precipitation, membrane filtration, solvent extraction, electrodialysis, ion exchange and adsorption are applicable for the removal of heavy metals from aqueous solutions [30–34]. Ion exchange usually requires a high capital investment for the equipment as well as high operational cost [35]. However, only the adsorption method is the most versatile and widely used, because the traditional methods are more expensive and least feasible for small-scale industries [36,37]. A wide variety of porous materials, such as agricultural waste, polymers, clay minerals and carbon materials have been investigated as adsorbents for the removal of toxic metals [38]. In recent years, molecular imprinting (MI) adsorbents have been increasingly used in chromatographic separation, catalysis and sensing. But up to our knowledge, limited studies have been carried on to the removal and recovery of heavy metals from waste streams [39,40]. These nanomaterials are very effective as a separation medium for water purification as they have physicochemical properties such as the high surface area to mass ratio due to decreased size and material dimension that leads to the availability of a large number of atoms or molecules on the surface to enhance the adsorption of contaminants [41–43].

2. Mechanism for synthetic process of molecular imprinted nanomaterials

2.1. General principle

Molecular imprinting of synthetic polymers is a process where functional and cross-linking monomers are copolymerized in the presence of the analyte (imprint molecule), which acts as a molecular template [44]. The functional monomers initially form a complex with the imprint molecule, and following polymerization, their functional groups are held in