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Review

Heavy metal removal from water/wastewater by nanosized metal oxides: A review

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ABSTRACT

Nanosized metal oxides (NMOs), including nanosized ferric oxides, manganese oxides, aluminum oxides, titanium oxides, magnesium oxides and cerium oxides, provide high surface area and specific affinity for heavy metal adsorption from aqueous systems. To date, it has become a hot topic to develop new technologies to synthesize NMOs, to evaluate their removal of heavy metals under varying experimental conditions, to reveal the underlying mechanism responsible for metal removal based on modern analytical techniques (XAS, ATR-FT-IR, NMR, etc.) or mathematical models, and to develop metal oxide-based materials of better applicability for practical use (such as granular oxides or composite materials). The present review mainly focuses on NMOs' preparation, their physicochemical properties, adsorption characteristics and mechanism, as well as their application in heavy metal removal. In addition, porous host supported NMOs are particularly concerned because of their great advantages for practical application as compared to the original NMOs. Also, some magnetic NMOs were included due to their unique separation performance.

Contents

Abbreviations: NMOs, nanosized metal oxides; NFeOs, nanosized Fe oxides; NMnOs, nanosized Mn oxides; HFO, hydrous Fe oxides; HMO, hydrous Mn oxides; HAO, hydrous Al oxides; OMS, octahedral molecular sieve; TEM, transmission electron microscopy; BET, Brunauer–Emmett–Teller (triple-point N_2 Brunauer–Emmett–Teller adsorption isotherm); XRD, X-ray diffraction; XPS, X-ray photoelectron spectroscopy; VSM, vibrating sample magnetometer; pH_{pzc}, pH of zero point of charge.

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1. Introduction

Exposure to heavy metals, even at trace level, is believed to be a risk for human beings [1–4]. Thus, how to effectively and deeply remove undesirable metals from water systems is still a very important but still challenging task for environmental engineers. Nowadays, numerous methods have been proposed for efficient heavy metal removal from waters, including but not limited to chemical precipitation, ion exchange, adsorption, membrane filtration and electrochemical technologies [5–9]. Among these techniques, adsorption offers flexibility in design and operation and, in many cases it will generate high-quality treated effluent. In addition, owing to the reversible nature of most adsorption processes, the adsorbents can be regenerated by suitable desorption processes for multiple use [10], and many desorption processes are of low maintenance cost, high efficiency, and ease of operation [11]. Therefore, the adsorption process has come to the forefront as one of the major techniques for heavy metal removal from water/wastewater.

Among the available adsorbents, nanosized metal oxides (NMOs), including nanosized ferric oxides, manganese oxides, aluminum oxides, titanium oxides, magnesium oxides and cerium oxides, are classified as the promising ones for heavy metals removal from aqueous systems [12–14]. This is partly because of their large surface areas and high activities caused by the size-quantization effect [15,16]. Recent studies suggested that many NMOs exhibit very favorable sorption to heavy metals in terms of high capacity and selectivity, which would result in deep removal of toxic metals to meet increasingly strict regulations [17]. However, as the size of metal oxides reduces from micrometer to nanometer levels, the increased surface energy inevitably leads to their poor stability. Consequently, NMOs are prone to agglomeration due to Van der Waals forces or other interactions [18], and the high capacity and selectivity of NMOs would be greatly decreased or even lost. Moreover, NMOs are unusable in fixed beds or any other flow-through systems because of the excessive pressure drops (or the difficult separation from aqueous systems) and poor mechanical strength. To improve the applicability of NMOs in real wastewater treatment, they were then impregnated into porous supports of large size to obtain composite adsorbents [10]. The widely used porous supports include activated carbon, natural materials, synthetic polymeric hosts, etc.

Besides traditional NMOs, magnetic NMOs attract increasing attentions because they can be easily separated from water under a magnetic field [19]. Also, magnetic NMOs-based composite adsorbents allowed easy isolation from aqueous solutions for recycling or regeneration [20]. Such facile separation is essential to improve the operation efficiency and reduce the cost during water/wastewater treatment.

This review presented a brief view on several typical NMOs, including their synthesis and characterization, their sorption behavior of heavy metals (e.g., Pb (II), Cd (II), Cr (VI), and Cu (II)) from aqueous systems under varying experimental conditions, the underlying mechanism responsible for the sorption, as well as their reusability. Porous host supported NMOs were briefly introduced according to the type of host materials, such as natural clay, membrane, and polymers. In addition, magnetic NMOs were summarized for their preparation and adsorptive performance on heavy metals.

2. Nanosized metal oxides

For adsorption of heavy metals from aqueous systems, the most widely studied NMOs include iron oxides, manganese oxides, aluminum oxides, and titanium oxides. They are present in different forms, such as particles, tubes and others (Table 1). The size and shape of NMOs are both important factors to affect their adsorption performance. Efficient synthetic methods to obtain shape-controlled, highly stable, and monodisperse metal oxide nanomaterials have been widely studied during the last decade. Generally, the synthesis methods can be classified into two categories: (1) physical approaches, including inert gas condensation, severe plastic deformation, high-energy ball milling, ultrasound shot peening, and (2) chemical approaches, including reverse micelle (or microemulsion), controlled chemical co-precipitation, chemical vapor condensation, pulse electrode position, liquid flame spray, liquid-phase reduction, gas-phase reduction, etc. [38]. Among these synthesis protocols, co-precipitation [39,40], thermal decomposition and/or reduction [41], and hydrothermal synthesis [42] techniques are used widely and are easily scalable with high yields [43]. As for the characterization of NMOs, research efforts focused on their characteristics, such as morphology, size, crystal structure, specific surface area and the pH of zero point of charge (pH_{pzc}). The most widely used techniques and tools for this purpose are summarized in Table 2.

In the following sections, recent advances in heavy metal removal from water and wastewater by NMOs are presented in terms of their synthesis, characterization, and application perspectives and are classified by the components of NMOs.

2.1. Nanosized ferric oxides

Iron is one of the most widespread elements in the earth. The facileness of resource and ease in synthesis render nanosized ferric oxides (NFeOs) to be low-cost adsorbents for toxic metal sorption. Since elemental iron is environmentally friendly, NFeOs can be pumped directly to contaminated sites with negligible risks of secondary contamination [51]. The intensively studied NFeOs for heavy metals removal from water/wastewater include goethite (α-FeOOH), hematite (α-Fe_2O_3) [21,22], amorphous hydrous Fe oxides [23], maghemite (γ-Fe_2O_3) [24,25], magnetite (Fe_3O_4) [19,44,52–55] and iron/iron oxide (Fe@Fe_xO_y) [50].

2.1.1. Goethite (α-FeOOH) and hematite (α-Fe_2O_3)

The chemical nature and the high specific surface area of goethite make it an efficient sorbent for metal cations [56]. Grossl et al. [21] evaluated the kinetics of Cu^{2+} adsorption/desorption on/from goethite (α-FeOOH) using the pressure-jump (p-jump) relaxation technique, which provides both kinetic and mechanistic information for reactions occurring on millisecond time scales. Adsorption of Cu (II) increased with the increasing pH from 4.5 to 5.5. The process was insensitive to the background electrolytes. Cu (II) sorption on nano-goethite surface was found to form an