

Review Article

Application of Metal Oxide Heterostructures in Arsenic Removal from Contaminated Water

Lei Chen,¹ Hongchuan Xin,¹ Yuan Fang,¹ Cong Zhang,¹ Feng Zhang,¹ Xing Cao,¹ Chunhui Zhang,² and Xuebing Li¹

¹ Key Laboratory of Biofuels, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China

² Henan Tianchen Environmental Protection Science & Technology Co., Ltd., Zhengzhou 450000, China

Correspondence should be addressed to Hongchuan Xin; xinhc@qibebt.ac.cn and Xuebing Li; lixb@qibebt.ac.cn

Received 10 December 2013; Accepted 2 January 2014; Published 18 February 2014

Academic Editor: Xiang Wu

Copyright © 2014 Lei Chen et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

It has become one of the major environmental problems for people worldwide to be exposed to high arsenic concentrations through contaminated drinking water, and even the long-term intake of small doses of arsenic has a carcinogenic effect. As an efficient and economic approach for the purification of arsenic-containing water, the adsorbents in adsorption processes have been widely studied. Among a variety of adsorbents reported, the metal oxide heterostructures with high surface area and specific affinity for arsenic adsorption from aqueous systems have demonstrated a promising performance in practical applications. This review paper aims to summarize briefly the metal oxide heterostructures in arsenic removal from contaminated water, so as to provide efficient, economic, and robust solutions for water purification.

1. Introduction

One of the decontamination goals is to detect and remove toxic substances from contaminated water in an affordable and robust way [1], because the widely distributed substances, such as heavy metals, are known to cause harm to humans and environments [2, 3]. Thus, how to effectively dispose of these environmentally undesirable substances from water systems is still very important and challenging. Numerous methods have been proposed for efficient heavy metal removal from water, including chemical precipitation, ion exchange, adsorption, membrane filtration, and electrochemical technologies, and so forth [4]. Among these techniques, as a simple, efficient, cost-effective, and ecofriendly approach for removing extremely toxic metal ions in drinking water and in hydrometallurgical streams, adsorption offers good flexibility in design and operation and will generate high-quality treated effluents for safe and healthy use [5]. The adsorption of heavy metals on solid adsorbents in dispersed form has been substantially studied [6–8], and the adsorption process has become one of the major methods for heavy metal removal from water. In general, for removing heavy

metal ions from water, an effective adsorbent should have the following features [9]: (i) rich active sites (ion exchange sites or vacancies); (ii) low cost; (iii) good mechanical property; and (iv) environmental friendliness. Furthermore, owing to the reversible nature of most adsorption processes, the adsorbents should be regenerated by suitable desorption processes with low maintenance cost, high efficiency, and easy operation.

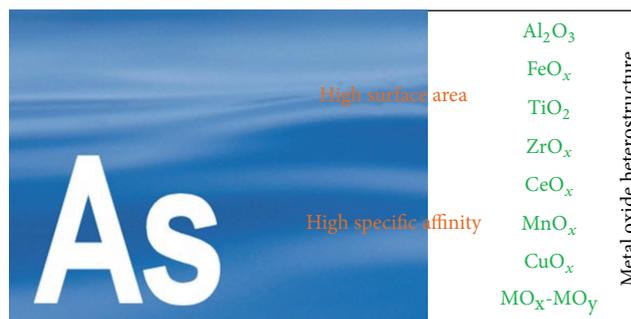
As a heavy metal with major environmental and health risk, the arsenic (As) disposal has brought about particular problems in case of anomalous concentration of As in ground and surface waters, because As with high mobility has the tendency to return to these waters [10]. Generally, natural waters contain low levels of total arsenic as As(V) and/or As(III) of 1–10 $\mu\text{g/L}$ [4, 10]. High arsenic concentrations can inhibit nitrification, and the inhibition of microorganisms in arsenate-rich soils is growing. Furthermore, arsenic is responsible for developing cancers of liver, bladder, skin, and kidney, and long-term intake of small doses of inorganic arsenic compounds may also cause many other diseases [6]. Similar to the techniques for disposing of other heavy metals as mentioned above, many approaches have also

been developed to remove As from contaminated water [11]. The arsenic disposal technologies can be specifically classified into three major categories: membrane separation, coagulation-precipitation, and adsorption [12, 13]. The interactions of arsenic species with metal oxides and hydroxides are important in order to control the mobility of arsenic in the natural environment, which can be used for removing arsenic with metal-based coagulants and adsorbents. For example, the prepared iron and aluminum based adsorbents from relatively inexpensive materials showed their effectiveness in removal of dissolved arsenic from water [14]. Actually, the capability and efficiency of adsorption technology in arsenic-containing water treatment mostly depend on the features and functions of the adsorbents employed.

The alumina and modified alumina adsorbents have been widely applied for As removal from aqueous systems, which is partly owing to their large surface areas and high activities [15, 16]. Other than alumina, the metal oxides with nanosized building blocks may contain high surface area and more surface functional groups, which can interact with As and other heavy metal ions [8]. The overall heterostructures of the metal oxides may also provide desirable mechanical properties, such as robustness, facile transportation, and easy recovery and regeneration, resulting in excellent adsorption capacities for As removal from contaminated water [17]. Note that the initial As ion concentrations are normally very low in practical applications; hence the capacity to remove As ions at low concentrations is a better criterion for selecting a suitable metal oxide adsorbent [18–20]. Moreover, the development of nanomaterials [9], especially those with heterogeneous structures, such as porous materials [21–24], spheres [25–31], hierarchical materials [32–36], nanocomposites [37, 38], nanoparticles [39, 40], nanosheets [41–44], nanojunctions [45], nanowires [46, 47], nanoflowers [48], and binary metal oxides [49, 50], is expected to play a key role for the diversified applications, including the detection and remediation of water pollution. The design and application of novel nanostructured metal oxides has received more and more attention in the purification of arsenic contaminated water in the past few decades. The aim of this review is to present a broad view of metal oxide heterostructures as adsorbents that have been identified for use in arsenic removal from water systems.

2. Metal Oxide Heterostructures for Arsenic Removal

Arsenic is both redox sensitive and able to form oxyanions, so the speciation of arsenic is sensitive to both the redox states and pH values of the chemical environment. The most stable redox states include -3 (arsine gas, AsH_3), -1 (alkyl arsenic), 0 (elemental arsenic), $+3$ (arsenite), and $+5$ (arsenate), and the latter two states are dominant in aqueous arsenic solutions [11]. Once dissolved, both As(III) and As(V) species are able to bind with one or more hydrogen ions, forming two deprotonation series. The World Health Organisation's guideline for maximum arsenic concentration in drinking water is currently 10 ppb [14]. In the adsorption process for arsenic disposal, the heterostructured metal oxide based adsorbents mainly include activated alumina, iron oxides,



SCHEME 1: Schematic drawing of the main idea of the review paper.

zirconium oxides, titanium oxides, cerium oxides, binary metal oxides, and so on [5, 12]. Generally, the high surface area and high specific affinity for arsenic adsorption are the two key factors to determine the efficiency of arsenic removal from contaminated water. The high surface area of metal oxide may provide rich sites for arsenic adsorption, which is normally benefited from porous structures. The high specific affinity is mainly due to the abundant surface hydroxyls on metal oxides [5]. The schematic drawing to show the main idea of this review paper was illustrated in Scheme 1.

2.1. Activated Alumina. Activated alumina is the most commonly used adsorbent for arsenic removal from contaminated water [14, 16, 51, 52]. The activated alumina was applied successfully for removing arsenic, if the pH of wastewater was slightly acidic and the competing anions were present in small concentrations [12]. The activated alumina has the advantage of simple and long-time operation even for 1–3 months before regeneration is required. However, it is disadvantageous that both NaOH and H_2SO_4 are required in the regeneration process. Moreover, it is necessary to further treat and dispose of the spent contaminated alkaline and acid wastewaters.

The conventional activated alumina with ill-defined pore structures generally showed low adsorption capacities in a kinetically slow manner. An ideal activated alumina adsorbent should have accessible and interlinked pore systems, high surface area, and good physical and/or chemical stability. The arsenic removal was therefore carried out with a mesoporous alumina prepared *via* a templating method [53], and the resulting alumina was insoluble and stable under the condition of $\text{pH} = 3\text{--}7$. Compared with the conventional activated alumina, the maximum As(V) uptake of mesoporous adsorbent was ca. 7 times higher, and the adsorption kinetics were also more rapid. Surprisingly, the surface area of the adsorbent did not have influence on its adsorption capacity greatly. In this case, the key factor for adsorption was supposed to be uniform pore size and interlinked pore system. In a recent paper, Han et al. studied the mesoporous alumina as an effective adsorbent for arsenic(V) removal in the pH of 2.5–7.0 [51]. The arsenic adsorption data were well fitted by the Langmuir isotherm model with a maximum adsorption capacity of 36.6 mg/g at near neutral pH. The mesoporous structure was favorable for the diffusion and transportation of arsenate species, and the high surface

area and more hydroxyl groups benefited the formation of positive aluminum hydroxide species. Li et al. also reported a highly ordered mesoporous alumina with superb arsenic removal capacities, which could reduce the arsenic concentration from 100 ppb to less than 10 ppb [52], suggesting that the ordered mesoporous alumina could become the ideal adsorbents in the practical application of water purification.

2.2. Iron Oxides. Iron is one of the most widespread elements in the earth. The convenience of resource and ease in synthesis renders iron oxides as environmentally friendly and low-cost adsorbents for arsenic adsorption [8].

The iron oxide-coated sand with an easy preparation procedure was investigated for its performance to remove arsenic in water [54, 55]. The adsorption reaction showed a Langmuir-type adsorption isotherm, where the electrostatic interaction was possibly involved in the adsorption. Recently, the iron-oxide coated natural rock was developed with As(III) adsorptive capacity of 1.647 mg/g [56], which was in accordance with the data evaluated from the Langmuir isotherm.

The ultrafine α -Fe₂O₃ nanoparticles were prepared to remove arsenic ions from both lab-prepared and natural waters [39]. These α -Fe₂O₃ nanoparticles were aggregated into a highly porous structure with a high specific surface area of 162 m²/g, and high-affinity hydroxyl groups were covered on the surface. Under neutral pH, the adsorption capacities of the α -Fe₂O₃ nanoparticles for As(III) and As(V) from lab-prepared water samples were found to be ca. 95 mg/g and 47 mg/g, respectively. These α -Fe₂O₃ nanoparticles maintained their arsenic adsorption capacity even at very high competing anion concentrations. Moreover, without the peroxidation and/or the pH adjustment, these α -Fe₂O₃ nanoparticles could effectively remove both As(III) and As(V) from a contaminated natural lake water sample [39]. Fe₂O₃ showed a higher capacity than that of Al₂O₃ in the removal of As(V) ions from water, and the initial sorption rate of Fe₂O₃ was also higher than that of Al₂O₃, which indicated that the nano-Fe₂O₃ is effective in the removal of As(V). The flower-like hierarchical iron oxides were used for removal of As(V) ions [17, 57]. The As(V) adsorption capacity of 5.3 mg/g with all three types of iron oxides (α -Fe₂O₃, γ -Fe₂O₃, and Fe₃O₄) was obtained, which was about 10 times higher than that of a commercial iron oxide sample (0.46 mg/g).

Mesoporous magnetic nanostructures may solve the problems associated with aggregation and poor separation. The mesoporous γ -Fe₂O₃ was therefore developed with a specific surface area of 35.7 m²/g, demonstrating a maximum uptake of arsenic ions of 73.2 mg/g, which was higher than that of the aggregated γ -Fe₂O₃ nanoparticles [58]. This was mainly attributed to the larger specific surface area, pore volume, and pore sizes of the mesoporous γ -Fe₂O₃ structures.

Mamindy-Pajany et al. studied the arsenic adsorption by commercially available goethite and haematite [59]. Higher adsorption was observed in acidic pH, and the adsorption on both adsorbents decreased at alkaline pH values. There was no effect of the ionic strength on arsenate adsorption, implying the formation of an inner-sphere surface complex.

At pH values corresponding to natural water, both haematite and goethite were able to adsorb more than 80% of arsenic, irrespective of the initial concentration. The iron oxides used were supposed to be suitable adsorbents for As(V) removal technologies. Later, Mamindy-Pajany et al. also discussed arsenic(V) adsorption under different physicochemical conditions with the commercial adsorbents: hematite, goethite, and magnetite [60]. The arsenate adsorption was related to the iron content of adsorbents, and the adsorption rate increased in the following order: goethite > hematite > magnetite. The arsenate adsorption was fitted well by the Langmuir model for almost all adsorbents, indicating a monolayer adsorption of arsenic.

Babu et al. reported that the adsorbed arsenic on magnetic Fe₃O₄ core-shell nanorods was easily removed by magnetic separation and regenerated by acid treatment, resulting in an arsenic removal rate of more than 99% [29]. Feng et al. synthesized superparamagnetic acid-coated Fe₃O₄ nanoparticles with a high specific surface area through an environmentally friendly hydrothermal route, which exhibited a maximum adsorption capacity of 16.56 mg/g for arsenic(V) and 46.06 mg/g for arsenic(III) [61]. The adsorption data were in accordance with the Langmuir equation. In another study, the low-cost Fe₃O₄-loaded activated carbon as adsorbent was developed with Fe₃O₄ nanoparticles uniformly deposited on the surface of the composite, presenting a high surface area of 349 m²/g and a pore volume of 0.20 cm³/g [62]. The higher temperature favored the adsorption capacity, and the composite displayed an excellent adsorption capability for arsenate with a maximum adsorption capacity of 204.2 mg/g at pH 8.0. Furthermore, the magnetization of composite allowed an easy regeneration by an external magnetic field after the adsorption process.

2.3. Titanium Oxides. As an important oxide with numerous practical industrial applications, titanium oxides (TiO₂, also called titania) have attracted significant attention in the fields of photocatalysis, lithium ion batteries, and wastewater purification [63].

The nanocrystalline TiO₂ exhibited a much higher adsorption capacity for As(V) and As(III) than fumed TiO₂ (Degussa P25) and granular ferric oxide [64]. Over 0.5 mmol/g of As(V) and As(III) was adsorbed by TiO₂ at an equilibrium arsenic concentration of 0.6 mmol/L. The competing anions showed a moderate effect on the As(III) and As(V) adsorption capacities of TiO₂ within neutral pH range. The authors also investigated the arsenate [As(V)] and arsenite [As(III)] interactions at the solid-water interface of nanocrystalline TiO₂ by using electrophoretic mobility measurements, Fourier transform infrared spectroscopy, extended X-ray absorption fine structure spectroscopy, and surface complexation modeling [19]. Jing et al. studied the adsorption of organic arsenic, such as monomethylarsonic acid and dimethylarsinic acid, on nanocrystalline TiO₂ [65] and found that bidentate and monodentate inner-sphere complexes were formed with the TiO₂ surface during the adsorption. Jézéquel and Chu analyzed the effects of pH and divalent cations on the adsorption of arsenate (As(V)) by TiO₂ nanoparticles [66].

Highly nanoporous titania spheres were prepared through *in situ* hydrolysis of titanium glycolate precursor spheres [20]. In case of the initial As(V) concentration of 184.8 ppm, the removal capacity of the titania spheres was 51.8 mg/g, much higher than commercial and directly calcined samples. The As(V) removal was proposed to form bidentate binuclear surface complexes between TiO₂ and As(V) species in the solution. Guo et al. reported a three-dimensional TiO₂ nanostructure consisting of a nanoparticle core and needlelike surface, demonstrating a maximum adsorption capacity of 59.7 mg/g for As(V) [67]. The high performance of self-assembled TiO₂ in water treatment was due to the large hydroxyl group density, high specific surface area, and the three-dimensional nanostructure consisting of a nanoparticle core and needlelike surface.

2.4. Zirconium Oxides. Zirconium-based oxides are stable, nontoxic, and not dissolvable in water, so they are an attractive choice for arsenic removal in drinking water [68, 69].

The zirconium oxide nanoparticles with high adsorption capacities for both As(III) and As(V) at near neutral pH were developed [68, 70]. These ZrO₂ nanoparticles could remove arsenic species even with exceptionally high concentrations of competing ions. Based on this, highly porous and nanostructured ZrO₂ spheres were then fabricated, showing better arsenic removal performance on both As(III) and As(V) than ZrO₂ nanoparticles [71], which was readily applied to conventional fixed-bed adsorption reactors in industry. These zirconium oxide spheres are nontoxic, highly stable, and resistant to acid and alkali, with a high arsenic adsorption capacity. The ZrO₂ spheres had a promising potential for their application in water treatment practice.

A commercially available mesoporous hydrous zirconium oxide was employed for arsenic removal, and some competitive anions and cations were studied under batch and column conditions [69, 72]. The exchange performance of the hydrous zirconium oxide was pH-dependent. The adsorbent exhibited high adsorption capacity at pH < 8. It was found that the silicate (and phosphate) ions were the main competitors affecting the arsenic removal from drinking water or groundwater. The results of field trials showed high efficiency of the mesoporous hydrous zirconium oxide for treating arsenic contaminated water.

The Zr(IV)-loaded phosphoric acid chelating resin was synthesized, showing a maximum As(V) adsorption capacity of approximately 0.20 mmol/mL for wet resin (0.67 mmol/g for dry resin) [73]. It was found that NaCl and NaNO₃ could enhance the adsorption of As(V), and the electrolytes in seawater also promoted the adsorption of As(V). In addition, the Zr-containing resin displayed high selectivity to As(III). Seko et al. reported a fibrous adsorbent prepared by loading zirconium on fibrous phosphoric adsorbent with a zirconium density of 4.1 mmol/g [74], displaying a total As(V) adsorption capacity of 2.0 mmol/g at pH = 2. Its superb adsorption rate was 130 times faster and its capacity was 6 times higher than those of adsorbent resin.

Hristovski et al. synthesized nanoporous ZrO₂ spheres by the impregnation of macroporous ion-exchange media with zirconium salt followed by high temperature treatment, and

the fabricated ZrO₂ spheres exhibited the adsorption capacity comparable to some commercially available iron oxides [75]. Moreover, the high porosity was provided for improved pore diffusion and faster mass transfer, which may be critical for applications when diffusion is a limiting factor. However, due to the higher production cost than iron based oxides, the ZrO₂ spheres may be limited to specific applications where iron based oxides could not be used efficiently. Suzuki et al. reported a porous resin loaded with monoclinic or cubic hydrous zirconium oxide prepared by incorporation of ZrOCl₂ into porous spherical polymer beads, which presented maximum arsenic adsorption capacities of ca. 1.5 and 1.2 mmol/g for As(III) and As(V), respectively [76]. The hydrous zirconium oxide-loaded resin displayed a strong adsorption for As(V) in the range of slightly acidic to neutral conditions, while As(III) was favorably adsorbed at pH of 9–10. This approach was supposed to be applicable for various combinations of hydrous metal oxides and porous matrices of desired applications.

2.5. Cerium Oxides. Cerium oxide was widely studied, because it is one of the most abundant and least expensive rare earth metal oxides. Cerium oxide possesses the lowest solubility against acid among the rare earth metal oxides and does not elute in the process of removing harmful ions in water [77, 78]. Therefore, it is believed to be a very promising alternative adsorbent in arsenic disposal.

For the ceria used as the adsorbent for As removal, a 3D flowerlike micro/nanocomposite structure of ceria resulted in much higher removal capacities than the commercial metal oxides [18]. The larger surface area of heterostructured cerium oxides may explain both higher removal capacities and faster adsorption rates. About 90% of the adsorption capacity was reached quickly after mixing ceria and As(V) solution.

Li et al. synthesized hydrous cerium oxide nanoparticles with a high specific surface area of 198 m²/g and high affinity surface hydroxyl group by a simple precipitation process, and it demonstrated exceptional adsorption properties in terms of adsorption capacity and kinetics on both As(III) and As(V) [78]. At neutral pH, their arsenic adsorption capacity was over 170 mg/g for As(III) and 107 mg/g for As(V), respectively. Even at very low equilibrium arsenic concentrations, the amount of As(III) and As(V) adsorbed by the nanoparticles was still more than 13 mg/g at 10 μg/L and 40 mg/g at 50 μg/L, respectively, which were higher than the arsenic adsorption capacities for most commercial adsorbents. Over a wide pH range of 3–11, the nanoparticles could efficiently remove As(III) by adsorption. Such exceptional arsenic adsorption performance by the cerium oxide nanoparticles was shown to derive from the strong inner-sphere complexation [78]. Meanwhile, the same group also prepared a novel composite adsorbent by integrating CeO₂ nanoparticles into silica monoliths [79]. The composite demonstrated superior arsenic removal performance on both lab-prepared and natural water samples. After desorption and regeneration, the composite still maintained a good arsenic adsorption performance, which was promising for their potential industrial applications.

2.6. Manganese Oxides. Manganese oxide is an important natural oxidizing agent. The As(III) oxidation by manganese oxide is very vital in both the natural cycling of As and the development of remediation technology, which can be used to lower the concentration of dissolved As(III) in drinking water [80].

The reactivity of As(III) with a synthetic MnO_2 compound was investigated to provide some new insights into the reaction of As(III) with a representative synthetic birnessite [81]. The studies found that the As(V)- MnO_2 complex formed was most likely a bidentate binuclear corner sharing (bridged) complex occurring at MnO_2 crystallite edges and interlayer domains. Moreover, the As(III) oxidation caused a surface alteration, creating fresh reaction sites for As(V) adsorption on MnO_2 surfaces. Zhu et al. investigated As(V) and As(III) surface complex structures and reaction energies on both Mn(III) and Mn(IV) sites with the density functional theory calculations in order to better understand As(III) oxidation by a layered MnO_2 mineral birnessite [82]. It was then hypothesized that the Mn(III) sites were less reactive in terms of As(III) oxidation due to their lower affinity for As(III) adsorption, higher potential blocked by As(V) complexes, and slower electron transfer rates with adsorbed As(III).

Li et al. used the pyrolusite ($\alpha\text{-MnO}_2$) to investigate the oxidation of arsenite into arsenate with batch experiments [83]. The arsenite transformation was accompanied by the adsorption and fixation of both As(III) and As(V) on $\alpha\text{-MnO}_2$. The enhancement on sodium arsenite oxidation may result from abundant active sites of $\alpha\text{-MnO}_2$. It was therefore proposed that $\alpha\text{-MnO}_2$ had important potential in arsenic transformation and removal as the environmentally friendly natural oxidant in contaminated water. Zhang and Sun synthesized multifunctional micro-/nanostructured MnO_2 spheres for the As removal from water [84]. The batch experiments showed that As(III) species were effectively oxidized by the obtained MnO_2 followed by the adsorption of As(V) species. The As(V) removal rate with the MnO_2 spheres was clearly dependent on pH and ionic strength, and the coexisting anions such as CO_3^{2-} , SO_4^{2-} , and PO_4^{3-} could induce suppressive effects. The As(III) and As(V) interacted differently with the synthesized MnO_2 spheres.

2.7. Copper Oxides. CuO is an effective arsenic adsorbent because it does not require pH adjustments or oxidation of As(III) to As(V) and it performs well in the presence of competing anions. Cao et al. developed a hierarchically nanostructured CuO with high specific surface area through a facile two-step process [85]. The doughnut-like CuO structure possessed high removal capacity for As(III) and could be easily separated and recycled during water treatment processes. The removal capacities of different CuO samples were found to be proportional to their BET surface areas. The doughnut-like structure with an prominently larger specific surface area was therefore advantageous for As(III) removal. Martinson and Reddy synthesized CuO nanoparticles with a surface area of $85 \text{ m}^2/\text{g}$ [86], and the nanoparticles could effectively remove As(III) and As(V) at pH 6–10, with a

maximum adsorption capacity of 26.9 mg/g for As(III) and 22.6 mg/g for As(V). The presence of sulfate and silicate in water did not inhibit the As(V) adsorption but slightly inhibited the As(III) adsorption. The high concentrations of phosphate ($>0.2 \text{ mmol/L}$) reduced the arsenic adsorption by CuO nanoparticles.

2.8. Magnesium Oxide. Magnesium oxide was utilized as a sorbent in water treatment to remove toxic ions and organic pollutants, but the studies on arsenic removal by MgO are still very limited. Hristovski et al. reported the removal of As(V) by commercial MgO powders [87]. Liu et al. demonstrated highly porous magnesium oxide nanoflakes with a high surface area of $115.9 \text{ m}^2/\text{g}$ and a total pore volume of ca. $0.254 \text{ cm}^3/\text{g}$ [88]. The MgO adsorbents displayed an exceptional As(III) removal performance from aqueous solutions with a maximum adsorption capacity of 506.6 mg/g . The high As(III) adsorption capacity was dependent on the *in situ* formation of Mg(OH)_2 due to the interaction of MgO nanoflakes with water. The formed Mg(OH)_2 could form a magnesium-arsenite compound, which was responsible for the high affinity to As(III) in aqueous solution.

2.9. Binary Metal Oxides. Compared with the metal oxides based on a single metal, the binary oxides based on two or more metals (or elements) may provide promoted performance for arsenic disposal from contaminated water. We hereby summarized some typical binary metal oxides with superior arsenic adsorption performance.

Three types of aluminosilicates (natural metakaoline, natural clinoptilolite-rich tuff, and synthetic zeolite) treated with Fe(II) nanoparticles were employed for the arsenate sorption from model aqueous solution [89]. The sorption capacity of Fe(II)-treated adsorbents was increased significantly in comparison to the untreated material with the As removal rate of over 95%. Li et al. used an iron(III) exchanged natural zeolite clinoptilolite to enhance As removal [90]. The batch test showed a sorption capacity of 144 mmol/kg on the Fe(III)/zeolite, and the As adsorption could reach up to 100 mg/kg . Bilici Baskan and Pala modified the clinoptilolite with 0.1 M FeCl_3 , and at lower initial arsenate concentration, the adsorbent exhibited greater removal rates [91]. This study showed that the adsorbed amount of arsenic was dependent on both the iron concentration in the clinoptilolite and the initial arsenate concentrations.

The Fe-Zr oxides have attracted much attention in the treatment of arsenic-containing water. Gupta et al. synthesized a nanostructured iron(III)-zirconium(IV) binary mixed oxide for arsenic removal [92]. The material could be regenerated (ca. 80%) with 2.0 M alkali solution after adsorption of arsenic. The toxicity characteristic leaching procedure test showed the nonhazardous nature of arsenic adsorbed material. Later, the same group reported an agglomerated nanostructured bimetal mixed iron(III)-zirconium(IV) oxide, exhibiting a good sorption capacity for arsenic(V) in $\text{pH} = 3.0\text{--}7.0$ [93]. The pseudo-second-order and the Langmuir isotherm equations could well explain the kinetic and equilibrium data ($\text{pH} = \text{ca. } 7.0$), respectively. The estimated

Langmuir monolayer capacity was ca. 9.4 mg g^{-1} . Zheng et al. prepared a zirconium-based magnetic sorbent with a surface area of $151 \text{ m}^2/\text{g}$, showing a maximum As adsorption capacity of 45.6 mg/g , which was much higher than many reported sorbents [94]. It was proposed that the $-\text{OH}$ groups played an important role in the uptake. Some of the arsenate was reduced to arsenite after its adsorption onto the magnetic sorbent. Ren et al. synthesized an iron-zirconium binary oxide adsorbent with a surface area of $339 \text{ m}^2/\text{g}$ by a coprecipitation method for both arsenate and arsenite removal [95]. The maximum adsorption capacities were 46.1 and 120.0 mg/g at pH 7.0 for both As(V) and As(III), respectively. Both As(V) and As(III) adsorption were well fitted by the pseudo-second-order equation. The characterization results indicated that the As(V) formed inner-sphere surface complexes, while As(III) formed both inner- and outer-sphere surface complexes at the interface of water/Fe-Zr binary oxide. The high uptake capability and good stability of the Fe-Zr binary oxide made it a potentially attractive adsorbent for the removal of both As(V) and As(III) from contaminated water.

The arsenate retention, sorption, and oxidation over Fe-Mn binary oxides may play an important role in the mobilization and transformation of arsenic, due to the common occurrence of these oxides in the environment. Zhang et al. synthesized Fe-Mn binary oxides [96] and found that the maximum As(V) sorption was observed at Mn/Fe ratio of 1/6, but the maximum As(III) uptake was at Mn/Fe ratio of 1/3. The Fe-Mn binary oxides represented attractive adsorbents for both As(V) and As(III) removal from water and groundwater. In another study, Shan and Tong fabricated magnetic Fe-Mn nanoparticles through heterogeneous nucleation technique [97], and at pH 7.0, 200 mg/L of As(III) could be easily decreased to below 10 mg/L by the Fe-Mn particles (0.1 g/L) within 20 min. The magnetic Fe-Mn oxides could be easily regenerated with ternary solution of NaOH, NaCl, and NaClO, and the adsorption and desorption efficiencies maintained above 98% and 87%, respectively, after 5 consecutive cycles.

The Fe-Ce bimetal oxide adsorbents were prepared by a coprecipitation method [98, 99], and the Fe-Ce oxides released $0.15\text{--}0.24 \text{ mmol}$ of sulfate for every mmol of arsenate adsorbed, suggesting that the surface hydroxyl groups were the major active sites, and sulfate groups might play a role for the adsorption [100]. The arsenate adsorbed on the used Fe-Ce oxides could be desorbed with an efficiency of 89% using 1.0 M NaOH, and the regenerated Fe-Ce oxides after desorption showed similar arsenate adsorption performance to the fresh one. Dou et al. investigated the As(V) adsorption mechanism on an Fe-Ce bimetal oxide [101], finding that the monodentate mononuclear and bidentate binuclear As surface complexes coexisted in the system. Compared with the dominant bidentate binuclear complex for As existing on iron (hydro)oxides in other reports, the existence of the monodentate complex could be explained by the incorporation of Ce atoms and the high surface loading. Basu and Ghosh reported nanostructured Fe(III)-Ce(IV) mixed oxides with a surface area of $104 \text{ m}^2/\text{g}$ [102], and the As(III)-sorption capacity of the bimetal mixed oxide was nominally influenced

by the presence of the groundwater occurring ions in the reaction system.

The ultrafine superparamagnetic Fe-Mg nanocrystallites were synthesized by Mg-doping of $\alpha\text{-Fe}_2\text{O}_3$ in a solvent thermal process [103]. The nanocrystallites greatly improved the arsenic adsorption performance in both lab-prepared and natural water samples at near neutral pH, mainly due to the increased surface area, enhanced dispersion, and contact with arsenic species in water by Mg doping. This study may offer a simple and efficient one-step treatment option for arsenic contaminated water without the pre-/posttreatment, which is required for current industrial processes. The concept of electronegativity (EN) is widely used in physics, chemistry, and materials science, and it is an important parameter in describing the nature of chemical bonds and further explaining the structure and properties of materials. Recently, various electronegativity and chemical bonds were shown in alloy $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ($x = 0.0\text{--}1.0$) based on calculation [104], which might be promising in the removal of arsenic.

The manganese oxide-coated-alumina was used for As(III) removal in drinking water [105]. The predicted maximum As(III) sorption capacity was 42.48 mg/g , which was considerably higher than that of activated alumina (20.78 mg/g). The sorption kinetics followed a pseudo-second-order equation. The As(III) removal mechanism was proposed to undergo a two-step process, that is, oxidation of As(III) to As(V) and retention of As(V) on the adsorbent surface to form an inner surface complex.

A nanostructured Fe-Cu binary oxide was synthesized via a facile coprecipitation method as a facile, efficient, and low-cost adsorbent for arsenic removal from water [106]. The Fe-Cu binary oxide with a Cu/Fe molar ratio of 1/2 displayed excellent performance in removing both As(V) and As(III) from water, with the maximal adsorption capacities for As(V) and As(III) of 82.7 and 122.3 mg/g at pH 7.0, respectively. The presence of sulfate and carbonate showed no significant effect on arsenic removal, but the phosphate obviously inhibited the arsenic disposal, especially at high concentrations. Furthermore, the Fe-Cu binary oxide could be used repeatedly after regeneration with NaOH solution.

The nanostructured Ce-Mn oxide materials were prepared by redox conversion coprecipitation and sol-gel methods, showing a good efficiency of arsenic removal at neutral pH and room temperature [107].

3. Conclusion

Water is the dominant pathway of arsenic exposure. Based on their abundance and adsorption capacity, metal oxides with heterostructures have become one of the most promising adsorbents for the arsenic removal from aqueous solutions. The well-known and currently used industrial metal oxides for arsenic remediation include ferric oxide and aluminum oxide. Industrially, the cost considerations make it expedient to use local materials as adsorbents for arsenic removal [108]. The stabilisation/solidification processes are currently used to treat industrial wastes containing As [11]. The lime neutralization accompanied by coprecipitation of arsenic

with ferric iron is the industrial choice for arsenic removal from acidic mineral processing effluents [109].

Some important progresses have been made on metal oxides as adsorbents for arsenic disposal. The metal oxides shall have the features of being robust, nontoxic, easily available, and cost-effective. As discussed in the review paper, the metal oxide heterostructures, including activated alumina, iron oxide, titanium oxide, zirconium oxide, manganese oxide, and binary metal oxides, fit these criteria well. However, from a practical point of view, the treatment of arsenic contaminated water with metal oxides still has a long way to go. Note that the adsorption techniques often require controlling pH and considering the final disposal of arsenic-contaminated residues.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

This project was sponsored by the Qingdao Key Technology Program (nos. 12-1-3-68-nsh, 13-1-3-123-nsh, and 13-4-4-25-chg).

References

- [1] M. A. Shannon, P. W. Bohn, M. Elimelech, J. G. Georgiadis, B. J. Marias, and A. M. Mayes, "Science and technology for water purification in the coming decades," *Nature*, vol. 452, no. 7185, pp. 301–310, 2008.
- [2] B. Jia, W. Jia, F. Qu, and X. Wu, "General strategy for self assembly of mesoporous SnO₂ nanospheres and their applications in water purification," *RSC Advances*, vol. 3, no. 30, pp. 12140–12148, 2013.
- [3] J. Wang, F. Qu, and X. Wu, "Photocatalytic degradation of organic dyes with hierarchical Ag₂O/ZnO heterostructures," *Science of Advanced Materials*, vol. 5, no. 10, pp. 1364–1371, 2013.
- [4] M. C. F. Magalhães, "Arsenic. An environmental problem limited by solubility," *Pure and Applied Chemistry*, vol. 74, no. 10, pp. 1843–1850, 2002.
- [5] J. QU, "Research progress of novel adsorption processes in water purification: a review," *Journal of Environmental Sciences*, vol. 20, no. 1, pp. 1–13, 2008.
- [6] T. S. Y. Choong, T. G. Chuah, Y. Robiah, F. L. Gregory Koay, and I. Azni, "Arsenic toxicity, health hazards and removal techniques from water: an overview," *Desalination*, vol. 217, no. 1–3, pp. 139–166, 2007.
- [7] D. Mohan and C. U. Pittman Jr., "Arsenic removal from water/wastewater using adsorbents—a critical review," *Journal of Hazardous Materials*, vol. 142, no. 1–2, pp. 1–53, 2007.
- [8] M. Hua, S. Zhang, B. Pan, W. Zhang, L. Lv, and Q. Zhang, "Heavy metal removal from water/wastewater by nanosized metal oxides: a review," *Journal of Hazardous Materials*, vol. 211–212, pp. 317–331, 2012.
- [9] L. Zhang and M. Fang, "Nanomaterials in pollution trace detection and environmental improvement," *Nano Today*, vol. 5, no. 2, pp. 128–142, 2010.
- [10] P. L. Smedley and D. G. Kinniburgh, "A review of the source, behaviour and distribution of arsenic in natural waters," *Applied Geochemistry*, vol. 17, no. 5, pp. 517–568, 2002.
- [11] C. Sullivan, M. Tyrer, C. R. Cheeseman, and N. J. D. Graham, "Disposal of water treatment wastes containing arsenic—a review," *Science of the Total Environment*, vol. 408, no. 8, pp. 1770–1778, 2010.
- [12] J. Q. Jiang, "Removing arsenic from groundwater for the developing world—a review," *Water Science and Technology*, vol. 44, no. 6, pp. 89–98, 2001.
- [13] M. Vaclavikova, G. P. Gallios, S. Hredzak, and S. Jakabsky, "Removal of arsenic from water streams: an overview of available techniques," *Clean Technologies and Environmental Policy*, vol. 10, no. 1, pp. 89–95, 2008.
- [14] D. E. Giles, M. Mohapatra, T. B. Issa, S. Anand, and P. Singh, "Iron and aluminium based adsorption strategies for removing arsenic from water," *Journal of Environmental Management*, vol. 92, no. 12, pp. 3011–3022, 2011.
- [15] J. Hlavay and K. Polyák, "Determination of surface properties of iron hydroxide-coated alumina adsorbent prepared for removal of arsenic from drinking water," *Journal of Colloid and Interface Science*, vol. 284, no. 1, pp. 71–77, 2005.
- [16] H. Soner Altundogan, S. Altundogan, F. Tümen, and M. Bildik, "Arsenic removal from aqueous solutions by adsorption on red mud," *Waste Management*, vol. 20, no. 8, pp. 761–767, 2000.
- [17] J. S. Hu, L. S. Zhong, W. G. Song, and L. J. Wan, "Synthesis of hierarchically structured metal oxides and their application in heavy metal ion removal," *Advanced Materials*, vol. 20, no. 15, pp. 2977–2982, 2008.
- [18] L. S. Zhong, J. S. Hu, A. M. Cao, Q. Liu, W. G. Song, and L.-J. Wan, "3D flowerlike ceria micro/nanocomposite structure and its application for water treatment and CO removal," *Chemistry of Materials*, vol. 19, no. 7, pp. 1648–1655, 2007.
- [19] M. Pena, X. Meng, G. P. Korfiatis, and C. Jing, "Adsorption mechanism of arsenic on nanocrystalline titanium dioxide," *Environmental Science and Technology*, vol. 40, no. 4, pp. 1257–1262, 2006.
- [20] L. S. Zhong, J. S. Hu, L. J. Wan, and W. G. Song, "Facile synthesis of nanoporous anatase spheres and their environmental applications," *Chemical Communications*, vol. 44, no. 10, pp. 1184–1186, 2008.
- [21] C. Li, H. Zhang, D. Jiang, and Q. Yang, "Chiral catalysis in nanopores of mesoporous materials," *Chemical Communications*, vol. 43, no. 6, pp. 547–558, 2007.
- [22] Q. Yang, D. Han, H. Yang, and C. Li, "Asymmetric catalysis with metal complexes in nanoreactors," *Chemistry*, vol. 3, no. 8–9, pp. 1214–1229, 2008.
- [23] S. Rostamnia, H. Xin, X. Liu, and K. Lamei, "Simultaneously application of SBA-15 sulfonic acid nanoreactor and ultrasonic irradiation as a very useful novel combined catalytic system: an ultra-fast, selective, reusable and waste-free green approach," *Journal of Molecular Catalysis A*, vol. 374, pp. 85–93, 2013.
- [24] H. Xin, J. Liu, F. Fan et al., "Mesoporous ferrosilicates with high content of isolated iron species synthesized in mild buffer solution and their catalytic application," *Microporous and Mesoporous Materials*, vol. 113, no. 1–3, pp. 231–239, 2008.
- [25] X. Li, Y. Yang, and Q. Yang, "Organo-functionalized silica hollow nanospheres: synthesis and catalytic application," *Journal of Materials Chemistry A*, vol. 1, no. 5, pp. 1525–1535, 2013.
- [26] J. Liu, F. Liu, K. Gao, J. Wu, and D. Xue, "Recent developments in the chemical synthesis of inorganic porous capsules," *Journal of Materials Chemistry*, vol. 19, no. 34, pp. 6073–6084, 2009.

- [27] J. Liu and D. Xue, "Hollow nanostructured anode materials for Li-Ion batteries," *Nanoscale Research Letters*, vol. 5, no. 10, pp. 1525–1534, 2010.
- [28] B. Jia, W. Jia, Y. Ma, X. Wu, and F. Qu, "SnO₂ core-shell microspheres with excellent photocatalytic properties," *Science of Advanced Materials*, vol. 4, no. 7, pp. 702–707, 2012.
- [29] C. M. Babu, B. Palanisamy, B. Sundaravel, M. Palanichamy, and V. Murugesan, "A novel magnetic Fe₃O₄/SiO₂ core-shell nanorods for the removal of arsenic," *Journal of Nanoscience and Nanotechnology*, vol. 13, no. 4, pp. 2517–2527, 2013.
- [30] H. Yang, T. Zhou, and W. Zhang, "A strategy for separating and recycling solid catalysts based on the pH-triggered pickering-emulsion inversion," *Angewandte Chemie International Edition*, vol. 52, no. 29, pp. 7455–7459, 2013.
- [31] D. Wu, H. Zhu, C. Zhang, and L. Chen, "Novel synthesis of bismuth tungstate hollow nanospheres in water-ethanol mixed solvent," *Chemical Communications*, vol. 46, no. 38, pp. 7250–7252, 2010.
- [32] H. Xin, A. Koekkoek, Q. Yang, R. van Santen, C. Li, and E. J. M. Hensen, "A hierarchical Fe/ZSM-5 zeolite with superior catalytic performance for benzene hydroxylation to phenol," *Chemical Communications*, no. 48, pp. 7590–7592, 2009.
- [33] H. Xin, J. Zhao, S. Xu et al., "Enhanced catalytic oxidation by hierarchically structured TS-1 Zeolite," *Journal of Physical Chemistry C*, vol. 114, no. 14, pp. 6553–6559, 2010.
- [34] J. Zheng, Q. Zeng, Y. Zhang et al., "Hierarchical porous zeolite composite with a core-shell structure fabricated using β -zeolite crystals as nutrients as well as cores," *Chemistry of Materials*, vol. 22, no. 22, pp. 6065–6074, 2010.
- [35] H. C. Xin, X. P. Li, L. Chen, Y. Huang, G. R. Zhu, and X. B. Li, "Organosilane surfactant-directed synthesis of mesoporous zeolites," *Energy and Environment Focus*, vol. 2, no. 1, pp. 18–40, 2013.
- [36] A. J. J. Koekkoek, H. Xin, Q. Yang, C. Li, and E. J. M. Hensen, "Hierarchically structured Fe/ZSM-5 as catalysts for the oxidation of benzene to phenol," *Microporous and Mesoporous Materials*, vol. 145, no. 1–3, pp. 172–181, 2011.
- [37] C. Yan, L. Nikolova, A. Dadvand et al., "Multiple NaNbO₃/Nb₂O₅ Heterostructure nanotubes: a new class of ferroelectric/semiconductor nanomaterials," *Advanced Materials*, vol. 22, no. 15, pp. 1741–1745, 2010.
- [38] H. X. Wang, H. Q. Yang, H. R. Liu, Y. H. Yu, and H. C. Xin, "A mesoporous silica nanocomposite shuttle: pH-triggered phase transfer between oil and water," *Langmuir*, vol. 29, no. 22, pp. 6687–6696, 2013.
- [39] W. Tang, Q. Li, S. Gao, and J. K. Shang, "Arsenic (III,V) removal from aqueous solution by ultrafine α -Fe₂O₃ nanoparticles synthesized from solvent thermal method," *Journal of Hazardous Materials*, vol. 192, no. 1, pp. 131–138, 2011.
- [40] S. Rostamnia, A. Nuri, H. Xin, A. Pourjavadi, and S. H. Hosseini, "Water dispersed magnetic nanoparticles (H₂O-DMNPs) of gamma-Fe₂O₃ for multicomponent coupling reactions: a green, single-pot technique for the synthesis of tetrahydro-4H-chromenes and hexahydroquinoline carboxylates," *Tetrahedron Letters*, vol. 54, no. 26, pp. 3344–3347, 2013.
- [41] J. Wang, F. Qu, and X. Wu, "Synthesis of ultra-thin ZnO nanosheets: photocatalytic and superhydrophilic properties," *Science of Advanced Materials*, vol. 5, no. 8, pp. 1052–1059, 2013.
- [42] A. J. J. Koekkoek, W. Kim, V. Degirmenci, H. Xin, R. Ryoo, and E. J. M. Hensen, "Catalytic performance of sheet-like Fe/ZSM-5 zeolites for the selective oxidation of benzene with nitrous oxide," *Journal of Catalysis*, vol. 299, pp. 81–89, 2013.
- [43] C. Yan and D. Xue, "Novel self-assembled MgO nanosheet and its precursors," *Journal of Physical Chemistry B*, vol. 109, no. 25, pp. 12358–12361, 2005.
- [44] J. Zhao, M. Li, J. Sun et al., "Metal-oxide nanoparticles with desired morphology inherited from coordination-polymer precursors," *Chemistry*, vol. 18, no. 11, pp. 3163–3168, 2012.
- [45] J. H. Yang, D. G. Wang, H. X. Han, and C. Li, "Roles of cocatalysts in photocatalysis and photoelectrocatalysis," *Accounts of Chemical Research*, vol. 46, no. 8, pp. 1900–1909, 2013.
- [46] Y. Han, X. Wu, Y. Ma, L. Gong, F. Qu, and H. Fan, "Porous SnO₂ nanowire bundles for photocatalyst and Li ion battery applications," *CrystEngComm*, vol. 13, no. 10, pp. 3506–3510, 2011.
- [47] B. Wang, Y. Shi, and D. Xue, "Large aspect ratio titanate nanowire prepared by monodispersed titania submicron sphere via simple wet-chemical reactions," *Journal of Solid State Chemistry*, vol. 180, no. 3, pp. 1028–1037, 2007.
- [48] B. Jia, W. Jia, X. Wu, and F. Qu, "Hierarchical porous SnO₂ microflowers photocatalyst," *Science of Advanced Materials*, vol. 4, no. 11, pp. 1127–1133, 2012.
- [49] H. C. Xin, C. H. Liu, S. C. Zhang, L. Q. Wang, and S. G. Li, "Oxidation of CO over supported La-Sr-Cu mixed oxide catalysts," *Chinese Journal of Catalysis*, vol. 25, no. 9, pp. 727–730, 2004.
- [50] J. Zhao, Y. L. Zhang, P. P. Su, Z. X. Jiang, Q. H. Yang, and C. Li, "Preparation of Zn-Co-O mixed-metal oxides nanoparticles through a facile coordination polymer based process," *RSC Advances*, vol. 3, no. 12, pp. 4081–4085, 2013.
- [51] C. Y. Han, H. Y. Li, H. P. Pu et al., "Synthesis and characterization of mesoporous alumina and their performances for removing arsenic(V)," *Chemical Engineering Journal*, vol. 217, pp. 1–9, 2013.
- [52] W. Li, C. Y. Cao, L. Y. Wu, M. F. Ge, and W. G. Song, "Superb fluoride and arsenic removal performance of highly ordered mesoporous aluminas," *Journal of Hazardous Materials*, vol. 198, pp. 143–150, 2011.
- [53] Y. Kim, C. Kim, I. Choi, S. Rengaraj, and J. Yi, "Arsenic removal using mesoporous alumina prepared via a templating method," *Environmental Science and Technology*, vol. 38, no. 3, pp. 924–931, 2004.
- [54] A. Joshi and M. Chaudhuri, "Removal of arsenic from ground water by iron oxide-coated sand," *Journal of Environmental Engineering*, vol. 122, no. 8, pp. 769–771, 1996.
- [55] J. G. Huang and J. C. Liu, "Enhanced removal of As(V) from water with iron-coated spent catalyst," *Separation Science and Technology*, vol. 32, no. 9, pp. 1557–1569, 1997.
- [56] S. K. Maji, Y. H. Kao, P. Y. Liao, Y. J. Lin, and C. W. Liu, "Implementation of the adsorbent iron-oxide-coated natural rock (IOCNR) on synthetic As(III) and on real arsenic-bearing sample with filter," *Applied Surface Science*, vol. 284, pp. 40–48, 2013.
- [57] L. S. Zhong, J. S. Hu, H. P. Liang, A. M. Cao, W. G. Song, and L. J. Wan, "Self-assembled 3D flowerlike iron oxide nanostructures and their application in water treatment," *Advanced Materials*, vol. 18, no. 18, pp. 2426–2431, 2006.
- [58] Y. F. Lin and J. L. Chen, "Synthesis of mesoporous maghemite (gamma-Fe₂O₃) nanostructures with enhanced arsenic removal efficiency," *RSC Advances*, vol. 3, no. 35, pp. 15344–15349, 2013.
- [59] Y. Mamindy-Pajany, C. Hurel, N. Marmier, and M. Roméo, "Arsenic adsorption onto hematite and goethite," *Comptes Rendus Chimie*, vol. 12, no. 8, pp. 876–881, 2009.

- [60] Y. Mamindy-Pajany, C. Hurel, N. Marmier, and M. Roméo, "Arsenic (V) adsorption from aqueous solution onto goethite, hematite, magnetite and zero-valent iron: effects of pH, concentration and reversibility," *Desalination*, vol. 281, no. 1, pp. 93–99, 2011.
- [61] L. Feng, M. Cao, X. Ma, Y. Zhu, and C. Hu, "Superparamagnetic high-surface-area Fe_3O_4 nanoparticles as adsorbents for arsenic removal," *Journal of Hazardous Materials*, vol. 217–218, pp. 439–446, 2012.
- [62] Z. Liu, F.-S. Zhang, and R. Sasai, "Arsenate removal from water using Fe_3O_4 -loaded activated carbon prepared from waste biomass," *Chemical Engineering Journal*, vol. 160, no. 1, pp. 57–62, 2010.
- [63] D. H. Chen and R. A. Caruso, "Recent progress in the synthesis of spherical titania nanostructures and their applications," *Advanced Functional Materials*, vol. 23, no. 11, pp. 1356–1374, 2013.
- [64] M. E. Pena, G. P. Korfiatis, M. Patel, L. Lippincott, and X. Meng, "Adsorption of As(V) and As(III) by nanocrystalline titanium dioxide," *Water Research*, vol. 39, no. 11, pp. 2327–2337, 2005.
- [65] C. Jing, X. Meng, S. Liu et al., "Surface complexation of organic arsenic on nanocrystalline titanium oxide," *Journal of Colloid and Interface Science*, vol. 290, no. 1, pp. 14–21, 2005.
- [66] H. Jézéquel and K. H. Chu, "Enhanced adsorption of arsenate on titanium dioxide using Ca and Mg ions," *Environmental Chemistry Letters*, vol. 3, no. 3, pp. 132–135, 2005.
- [67] J. W. Guo, X. J. Cai, Y. Li, R. G. Zhai, S. M. Zhou, and P. Na, "The preparation and characterization of a three-dimensional titanium dioxide nanostructure with high surface hydroxyl group density and high performance in water treatment," *Chemical Engineering Journal*, vol. 221, pp. 342–352, 2013.
- [68] C. Hang, Q. Li, S. Gao, and J. K. Shang, "As(III) and As(V) adsorption by hydrous zirconium oxide nanoparticles synthesized by a hydrothermal process followed with heat treatment," *Industrial and Engineering Chemistry Research*, vol. 51, no. 1, pp. 353–361, 2012.
- [69] A. Bortun, M. Bortun, J. Pardini, S. A. Khainakov, and J. R. García, "Effect of competitive ions on the arsenic removal by mesoporous hydrous zirconium oxide from drinking water," *Materials Research Bulletin*, vol. 45, no. 11, pp. 1628–1634, 2010.
- [70] H. Cui, Q. Li, S. Gao, and J. K. Shang, "Strong adsorption of arsenic species by amorphous zirconium oxide nanoparticles," *Journal of Industrial and Engineering Chemistry*, vol. 18, no. 4, pp. 1418–1427, 2012.
- [71] H. Cui, Y. Su, Q. Li, S. Gao, and J. K. Shang, "Exceptional arsenic (III,V) removal performance of highly porous, nanostructured ZrO_2 spheres for fixed bed reactors and the full-scale system modeling," *Water Research*, vol. 47, no. 16, pp. 6258–6268, 2013.
- [72] A. Bortun, M. Bortun, J. Pardini, S. A. Khainakov, and J. R. García, "Synthesis and characterization of a mesoporous hydrous zirconium oxide used for arsenic removal from drinking water," *Materials Research Bulletin*, vol. 45, no. 2, pp. 142–148, 2010.
- [73] X. Zhu and A. Jyo, "Removal of arsenic(V) by zirconium(IV)-loaded phosphoric acid chelating resin," *Separation Science and Technology*, vol. 36, no. 14, pp. 3175–3189, 2001.
- [74] N. Seko, F. Basuki, M. Tamada, and F. Yoshii, "Rapid removal of arsenic(V) by zirconium(IV) loaded phosphoric chelate adsorbent synthesized by radiation induced graft polymerization," *Reactive and Functional Polymers*, vol. 59, no. 3, pp. 235–241, 2004.
- [75] K. D. Hristovski, P. K. Westerhoff, J. C. Crittenden, and L. W. Olson, "Arsenate removal by nanostructured ZrO_2 spheres," *Environmental Science and Technology*, vol. 42, no. 10, pp. 3786–3790, 2008.
- [76] T. M. Suzuki, J. O. Bomani, H. Matsunaga, and T. Yokoyama, "Preparation of porous resin loaded with crystalline hydrous zirconium oxide and its application to the removal of arsenic," *Reactive and Functional Polymers*, vol. 43, no. 1, pp. 165–172, 2000.
- [77] X. Peng, Z. Luan, J. Ding, Z. Di, Y. Li, and B. Tian, "Ceria nanoparticles supported on carbon nanotubes for the removal of arsenate from water," *Materials Letters*, vol. 59, no. 4, pp. 399–403, 2005.
- [78] R. Li, Q. Li, S. Gao, and J. K. Shang, "Exceptional arsenic adsorption performance of hydrous cerium oxide nanoparticles, part A: adsorption capacity and mechanism," *Chemical Engineering Journal*, vol. 185–186, pp. 127–135, 2012.
- [79] W. Sun, Q. Li, S. Gao, and J. K. Shang, "Exceptional arsenic adsorption performance of hydrous cerium oxide nanoparticles, part B: integration with silica monoliths and dynamic treatment," *Chemical Engineering Journal*, vol. 185–186, pp. 136–143, 2012.
- [80] W. Driehaus, R. Seith, and M. Jekel, "Oxidation of arsenate(III) with manganese oxides in water treatment," *Water Research*, vol. 29, no. 1, pp. 297–305, 1995.
- [81] B. A. Manning, S. E. Fendorf, B. Bostick, and D. L. Suarez, "Arsenic(III) oxidation and arsenic(V) adsorption reactions on synthetic birnessite," *Environmental Science and Technology*, vol. 36, no. 5, pp. 976–981, 2002.
- [82] M. Zhu, K. W. Paul, J. D. Kubicki, and D. L. Sparks, "Quantum chemical study of arsenic (III, V) adsorption on Mn-oxides: implications for arsenic(III) oxidation," *Environmental Science and Technology*, vol. 43, no. 17, pp. 6655–6661, 2009.
- [83] X.-J. Li, C.-S. Liu, F.-B. Li et al., "The oxidative transformation of sodium arsenite at the interface of $\alpha\text{-MnO}_2$ and water," *Journal of Hazardous Materials*, vol. 173, no. 1–3, pp. 675–681, 2010.
- [84] T. Zhang and D. D. Sun, "Removal of arsenic from water using multifunctional micro-/nano-structured MnO_2 spheres and microfiltration," *Chemical Engineering Journal*, vol. 225, pp. 271–279, 2013.
- [85] A.-M. Cao, J. D. Monnell, C. Matranga, J.-M. Wu, L.-L. Cao, and D. Gao, "Hierarchical nanostructured copper oxide and its application in arsenic removal," *Journal of Physical Chemistry C*, vol. 111, no. 50, pp. 18624–18628, 2007.
- [86] C. A. Martinson and K. J. Reddy, "Adsorption of arsenic(III) and arsenic(V) by cupric oxide nanoparticles," *Journal of Colloid and Interface Science*, vol. 336, no. 2, pp. 406–411, 2009.
- [87] K. Hristovski, A. Baumgardner, and P. Westerhoff, "Selecting metal oxide nanomaterials for arsenic removal in fixed bed columns: from nanopowders to aggregated nanoparticle media," *Journal of Hazardous Materials*, vol. 147, no. 1–2, pp. 265–274, 2007.
- [88] Y. Liu, Q. Li, S. Gao, and J. K. Shang, "Exceptional As(III) sorption capacity by highly porous magnesium oxide nanoflakes made from hydrothermal synthesis," *Journal of the American Ceramic Society*, vol. 94, no. 1, pp. 217–223, 2011.
- [89] B. Dousova, T. Grygar, A. Martaus, L. Fuitova, D. Kolousek, and V. Machovic, "Sorption of As-V on alumino silicates treated with Fe-II nanoparticles," *Journal of Colloid and Interface Science*, vol. 302, no. 2, pp. 424–431, 2006.
- [90] Z. Li, J. S. Jean, W. T. Jiang, P. H. Chang, C. J. Chen, and L. Liao, "Removal of arsenic from water using Fe-exchanged natural

- zeolite," *Journal of Hazardous Materials*, vol. 187, no. 1–3, pp. 318–323, 2011.
- [91] M. Bilici Baskan and A. Pala, "Removal of arsenic from drinking water using modified natural zeolite," *Desalination*, vol. 281, no. 1, pp. 396–403, 2011.
- [92] K. Gupta, K. Biswas, and U. C. Ghosh, "Nanostructure iron(III)-zirconium(IV) binary mixed oxide: synthesis, characterization, and physicochemical aspects of arsenic(III) sorption from the aqueous solution," *Industrial and Engineering Chemistry Research*, vol. 47, no. 24, pp. 9903–9912, 2008.
- [93] K. Gupta, T. Basu, and U. C. Ghosh, "Sorption characteristics of arsenic(V) for removal from water using agglomerated nanostructure iron(III)-zirconium(IV) bimetal mixed oxide," *Journal of Chemical and Engineering Data*, vol. 54, no. 8, pp. 2222–2228, 2009.
- [94] Y. M. Zheng, S. F. Lim, and J. P. Chen, "Preparation and characterization of zirconium-based magnetic sorbent for arsenate removal," *Journal of Colloid and Interface Science*, vol. 338, no. 1, pp. 22–29, 2009.
- [95] Z. Ren, G. Zhang, and J. P. Chen, "Adsorptive removal of arsenic from water by an iron-zirconium binary oxide adsorbent," *Journal of Colloid and Interface Science*, vol. 358, no. 1, pp. 230–237, 2011.
- [96] G. Zhang, H. Liu, J. Qu, and W. Jefferson, "Arsenate uptake and arsenite simultaneous sorption and oxidation by Fe-Mn binary oxides: influence of Mn/Fe ratio, pH, Ca^{2+} , and humic acid," *Journal of Colloid and Interface Science*, vol. 366, no. 1, pp. 141–146, 2012.
- [97] C. Shan and M. P. Tong, "Efficient removal of trace arsenite through oxidation and adsorption by magnetic nanoparticles modified with Fe-Mn binary oxide," *Water Research*, vol. 47, no. 10, pp. 3411–3421, 2013.
- [98] Y. Zhang, M. Yang, X. M. Dou, H. He, and D. S. Wang, "Arsenate adsorption on an Fe-Ce bimetal oxide adsorbent: role of surface properties," *Environmental Science and Technology*, vol. 39, no. 18, pp. 7246–7253, 2005.
- [99] Y. Zhang, M. Yang, and X. Huang, "Arsenic(V) removal with a Ce(IV)-doped iron oxide adsorbent," *Chemosphere*, vol. 51, no. 9, pp. 945–952, 2003.
- [100] Y. Zhang, X. M. Dou, M. Yang, H. He, C. Y. Jing, and Z. Y. Wu, "Removal of arsenate from water by using an Fe-Ce oxide adsorbent: effects of coexistent fluoride and phosphate," *Journal of Hazardous Materials*, vol. 179, no. 1–3, pp. 208–214, 2010.
- [101] X. Dou, Y. Zhang, B. Zhao, X. Wu, Z. Wu, and M. Yang, "Arsenate adsorption on an Fe-Ce bimetal oxide adsorbent: EXAFS study and surface complexation modeling," *Colloids and Surfaces A*, vol. 379, no. 1–3, pp. 109–115, 2011.
- [102] T. Basu and U. C. Ghosh, "Nano-structured iron(III)-cerium (IV) mixed oxide: synthesis, characterization and arsenic sorption kinetics in the presence of co-existing ions aiming to apply for high arsenic groundwater treatment," *Applied Surface Science*, vol. 283, pp. 471–481, 2013.
- [103] W. Tang, Y. Su, Q. Li, S. Gao, and J. K. Shang, "Mg-doping: a facile approach to impart enhanced arsenic adsorption performance and easy magnetic separation capability to $\alpha\text{-Fe}_2\text{O}_3$ nanoadsorbents," *Journal of Materials Chemistry A*, vol. 1, no. 3, pp. 830–836, 2013.
- [104] K. Li, Z. Ding, and D. Xue, "Composition dependence of bulk modulus and bond length of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ($x = 0.0 - 1.0$) alloy semiconductors," *Functional Materials Letters*, vol. 3, no. 4, pp. 241–244, 2010.
- [105] S. M. Maliyekkal, L. Philip, and T. Pradeep, "As(III) removal from drinking water using manganese oxide-coated-alumina: performance evaluation and mechanistic details of surface binding," *Chemical Engineering Journal*, vol. 153, no. 1–3, pp. 101–107, 2009.
- [106] G. S. Zhang, Z. M. Ren, X. W. Zhang, and J. Chen, "Nanostructured iron(III)-copper(II) binary oxide: a novel adsorbent for enhanced arsenic removal from aqueous solutions," *Water Research*, vol. 47, no. 12, pp. 4022–4031, 2013.
- [107] K. Gupta, S. Bhattacharya, D. Chattopadhyay et al., "Ceria associated manganese oxide nanoparticles: synthesis, characterization and arsenic(V) sorption behavior," *Chemical Engineering Journal*, vol. 172, no. 1, pp. 219–229, 2011.
- [108] V. K. Gupta, P. J. M. Carrott, M. M. L. Ribeiro Carrott, and S. Suhas, "Low-cost adsorbents: growing approach to wastewater treatment review," *Critical Reviews in Environmental Science and Technology*, vol. 39, no. 10, pp. 783–842, 2009.
- [109] Y. Jia, D. Zhang, R. Pan, L. Xu, and G. P. Demopoulos, "A novel two-step coprecipitation process using Fe(III) and Al(III) for the removal and immobilization of arsenate from acidic aqueous solution," *Water Research*, vol. 46, no. 2, pp. 500–508, 2012.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

