

Ionic Potential: A General Material Criterion for the Selection of Highly Efficient Arsenic Adsorbents



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[Manuscript received July 1, 2014, in revised form July 26, 2014, Available online 27 August 2014]

Arsenic is a highly toxic element and its contamination in water bodies is a worldwide problem. Arsenic adsorption with metal oxides/hydroxides-based adsorbents is an effective approach to remove arsenic species from water for the health of both human beings and the environment. However, no material criterion had been proposed for the selection of potential candidates. Equally puzzling is the fact that no clear explanation was available on the poor arsenic adsorption performance of some commonly used adsorbents, such as active carbon or silica. Furthermore, in-depth examination was also not available for the dramatically different competing adsorption effects of various anions on the arsenic adsorption. Through the arsenic adsorption mechanism study on these highly efficient arsenic adsorbents, we found that ionic potential could be used as a general material criterion for the selection of highly efficient arsenic adsorbents and such a criterion could help us to understand the above questions on arsenic adsorbents. This material criterion could be further applied to the selection of highly efficient adsorbents based on ligand exchange between their surface hydroxyl groups and adsorbates in general, which may be used for the prediction of novel adsorbents for the removal of various contaminations in water.

KEY WORDS: Arsenic adsorbents; Material selection criterion; Metal oxides/hydroxides; Ionic potential; Ligand exchange

1. Introduction

Arsenic is a highly toxic element and its contamination in water bodies is a worldwide problem, posing a great threat to human health and the quality of life^[1–4]. In natural water bodies, arsenic is usually found in two inorganic forms as As(III) (arsenite) and As(V) (arsenate), and As(III) is considerably more mobile and toxic than As(V)^[5]. Long-term exposure to arsenic from either contaminated drinking water, agriculture products irrigated by contaminated water, or direct exposure to contaminated water could cause a lot of health problems, including liver, lung, kidney, bladder, and skin cancers, cardio vascular system problem, and the retardation of mental development of children^[6,7]. The World Health Organization had classified arsenic as a carcinogen and recommended that its maximum

contaminant level (MCL) in drinking water should not be over 10 $\mu\text{g/L}$ to reduce its health risk to human beings^[8].

Adsorption is a commonly utilized technique in water treatment practice to remove contaminants from water, which is a surface-based process involving the adhesion of the adsorbate to the surface of the adsorbent^[5,9–11]. Compared with other arsenic removal techniques, the adsorption is considered as a promising process to remove arsenic contamination from aqueous environment because of its simplicity, cost-effectiveness, potential for regeneration, and sludge free operation, especially when the contamination concentration is very low^[5,9]. Accordingly, extensive research efforts had been made to develop highly efficient arsenic adsorbents^[12–15]. With the rapid development of nanotechnology, synthesized metal oxide/hydroxide nanoadsorbents had been developed in recent years, which demonstrated promising results on arsenic removal from aqueous environment due to their higher specific surface area and controllable surface properties suitable for arsenic removal^[16–22]. Several reviews had also been published recently, which summarized the significant progresses on the development of arsenic adsorbents, and identified several highly efficient arsenic adsorbent candidates, such as iron oxides/hydroxides, titanium oxides, zirconium oxides, and aluminum oxides^[5,9–11,23,24].

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<http://dx.doi.org/10.1016/j.jmst.2014.08.010>

However, most of these studies were focused on the synthesis, characterization, and arsenic adsorption performance evaluation of various adsorbents, while some of them further examined the adsorption mechanism of arsenic species onto these adsorbents. To the best of our knowledge, no effort had been made to examine the intrinsic material criterion for the selection of highly efficient arsenic adsorbents. It is still unclear why adsorbents demonstrate different arsenic adsorption performances even if they have similar surface areas, pore structures and the presence of surface hydroxyl groups, which had been identified as the factors to determine the arsenic adsorption performance of adsorbents^[12–22,25–29]. Equally puzzling is the fact that no clear explanation is available on the poor arsenic adsorption performance of some commonly used adsorbents, such as active carbon or silica, which had the proper pore structure, abundant surface hydroxyl groups, and even much larger surface area than reported highly efficient arsenic adsorbents^[5,30,31]. Furthermore, in-depth examination was also not available for the dramatically different competing adsorption effects of various anions on the arsenic adsorption, although this phenomenon had been observed by many research groups^[32–35].

In our recent work, several highly efficient arsenic adsorbents were developed, which demonstrated strong adsorption on both As(III) and As(V) species in natural water without the pre-treatment of oxidation and pH adjustment^[36–42]. Through the arsenic adsorption mechanism study on these highly efficient arsenic adsorbents, we found that ionic potential could be used as a general material criterion for the selection of highly efficient arsenic adsorbents and such a criterion could help us to understand the above questions on arsenic adsorbents. This material criterion could be further applied to the selection of highly efficient adsorbents based on ligand exchange between their surface hydroxyl groups and adsorbates in general, which may be used for the prediction of novel adsorbents for the removal of various contaminations in water.

2. Results and Discussion

The understanding of the arsenic adsorption process onto metal oxides/hydroxides in the molecular level is critical to determining the material criterion for the selection of high efficient arsenic adsorbents. Both macroscopic and microscopic techniques had been utilized by various research groups to elucidate the mechanism of arsenic adsorption onto metal oxides/hydroxides^[26,28,29,32–35,43–48]. It had been demonstrated that the strong arsenic adsorption onto several kinds of metal oxide/hydroxide adsorbents followed the inner-sphere complex mechanism. For example, extended X-ray absorption fine structure (EXAFS)^[48] and Fourier transform infrared spectroscopy (FTIR)^[49] studies of As(III) and As(V) at the goethite surface suggested their formation of inner-sphere bidentate binuclear bridging complexes. Pena *et al.*^[29] studied the adsorption mechanisms of As(III) and As(V) on nano-crystalline TiO₂ with EXAFS, FTIR and electrophoretic mobility measurement, which suggested that the adsorption of As(III) and As(V) onto TiO₂ followed the inner-sphere complex mechanism. Zhang *et al.*^[50] investigated the binding of As(III) to ferric hydroxide clusters using several density functional theory methods. The comparison of calculated and experimentally measured As–O and As–Fe bond distances indicated that As(III) forms both bidentate and monodentate corner-sharing complexes with Fe(III) octahedra. In our own work^[39], it was also demonstrated that the adsorption of both As(III) and As(V) onto ZrO₂ followed the inner-sphere

mechanism and the surface hydroxyl groups played the key role in arsenic adsorption by the combination of ionic strength effect analysis, FTIR, electrophoretic mobility measurement, and XPS analysis.

The arsenic adsorption mechanism study demonstrated that the arsenic adsorption onto metal oxides/hydroxides is a chemisorption process involving the ligand exchange between the surface hydroxyl groups on metal oxides/hydroxides and arsenic species in water, which depends on the competition between hydroxyl groups and arsenic species for the Lewis acid of the central ion (metal) of the metal oxides/hydroxides. Fig. 1 schematically demonstrates the adsorption of As(III) onto metal oxide surface, in which TiO₂ (200) was used as an example. The left side in Fig. 1 shows the before-adsorption status, while the right side shows the after-adsorption status. The desorption of surface hydroxyl groups is the first step in this process, which plays an important role in the arsenic adsorption process. The affinity of both surface hydroxyl groups and arsenic species to metal oxides/hydroxides is derived from the coordination complex of metallic ion (M) and oxygen ion (O), namely M–O bond, as shown in Fig. 1. If the M–O bond strength is very strong, it will be difficult for surface hydroxyl groups to be desorbed, which makes the adsorption of arsenic species difficult. On the other side, if the M–O bond strength is weak, no enough driving force could be supplied to adsorb either hydroxyl groups or arsenic species onto the surface. Therefore, there must be an optimum M–O bond strength range within which the adsorbents can have strong arsenic adsorption capacity. Thus, even with similar surface area, pore structure, and the presence of surface hydroxyl groups, different adsorbents demonstrate different arsenic adsorption performances due to this intrinsic material property difference.

Ionic potential (IP) is a simple approach to evaluate the M–O bond strength, which was firstly proposed by Cartledge in 1928, and is defined as an ion's charge divided by its radius (Å)^[51]. Ionic potential is thus a measure of charge density, which indicates how strongly or weakly a specific ion could be electrostatically attracted to ions with opposite charges, or be electrostatically repelled by ions with like charges. Fig. 2 shows the ionic potential map by ionic charge vs. ionic radius of various elements, which could be roughly divided into three regions and one transitional zone according to their ionic potential values. For cations, their ionic potential values vary largely, from ~0.75 for K⁺ to ~45 for N⁵⁺. In the region of IP < 3, oxides/hydroxides of cations with such low ionic potential values, for example K⁺ and Na⁺, are typically soluble because they only have weak bonds with O²⁻. In the region of IP > 12, cations with such high ionic potential values, for example N⁵⁺ and S⁶⁺, have strong bond with O²⁻ and form soluble oxocomplexes/oxohydroxocomplexes, for example NO₃⁻ or SO₄²⁻, because of

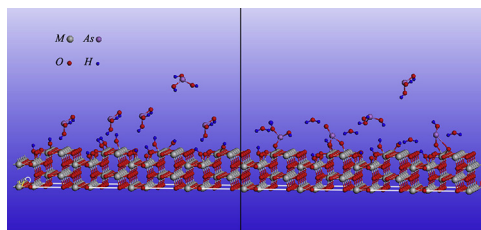


Fig. 1 Schematic illustration the adsorption of As(III) onto metal oxide surface, in which TiO₂ (200) was used as a metal oxide surface example.

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