Water treatment residuals containing iron and manganese oxides for arsenic removal from water – Characterization of physicochemical properties and adsorption studies

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HIGHLIGHTS

- Residuals from water deironing and demanganization were used as arsenic adsorbent.
- Waste material exhibited high sorption capacity of 132 mg As(III)/g and 77 mg As(V)/g.
- External diffusion of As(V) was rate-determining step of its adsorption.
- Rate-limiting step of As(III) removal was its oxidation prior to its adsorption.
- MnO_2 content in waste material enabled efficient As(III) removal in acidic conditions.

GRAPHICAL ABSTRACT
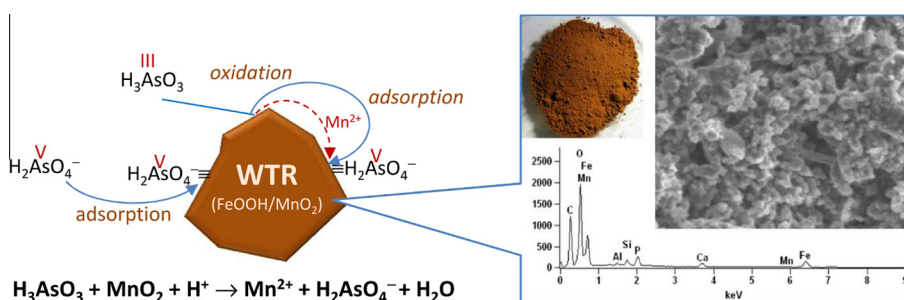
$$H_3AsO_3 + MnO_2 + H^+ \rightarrow Mn^{2+} + H_2AsO_4^- + H_2O$$

ARTICLE INFO

ABSTRACT

Water treatment residuals (WTRs), generated as a by-product during the deironing and demanganization process of infiltration water, were characterized and examined as arsenate and arsenite sorbent. The raw material consisted mainly of iron and manganese oxides with the ratio of Fe:Mn of 5:1. The adsorbent was also characterized by BET surface area measurement, X-ray diffraction (XRD), SEM EDS microscopy and X-ray photoelectron spectroscopy (XPS). The results showed that WTRs had a high surface area ($120 \, m^2 \, g^{-1}$) and were mainly amorphous, with small fractions of crystalline quartz and feroxyhyte. The maximum sorption capacities determined by means of the Langmuir isotherm equation were 132 mg As(III) g^{-1} and 77 mg As(V) g^{-1}. The higher arsenite uptake may be attributed to the creation of new adsorption sites at the solid surface as a result of As(III) oxidation. The XPS confirmed that arsenite was oxidized prior to adsorption, which was accompanied by release of Mn^{2+} cations followed by their adsorption on the sorbent surface. The effectiveness of arsenate removal decreased with the increase of pH, with a noticeable drop above pH_{pzc} of the sorbent, whereas arsenite adsorption was almost constant at acidic and neutral pH. A slight decrease was observed only above pH = 10 due to repulsion between the negatively charged surface of the sorbent and dissociated arsenites. The kinetic studies revealed that arsenate adsorption on WTRs was mainly controlled by external and intraparticle diffusion, whereas in the case of arsenites the two-step mechanism of the process influenced the rate of As(III) adsorption to a greater degree. The possibility of regeneration of the spent sorbent was also confirmed.

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1. Introduction

Arsenic is a highly toxic element classified as a Class A carcinogen by the International Agency for Research on Cancer. As a naturally occurring component of the environment it enters the aqueous systems by leaching from soils and minerals, causing a health risk in many regions of the world including North America, India and some European countries, where arsenic concentration in drinking water supplies exceeds 10 μg dm^{-3}, the maximum contaminant level (MCL) recommended by the WHO [1]. Over recent decades a significant effort has been made to evolve effective technologies of arsenic removal from water. Of the many approaches, adsorption seems to be the most promising, considering low arsenic concentrations in purified solutions. For this, various adsorbents have been used such as activated carbon, waste biomass sorbents, organic polymers, silica and much more selective metal oxides [2–7]. Their selectivity toward arsenic species is a result of the specific chemisorption mechanism based on formation of inner-sphere complexes between the adsorbate and adsorbent surface. Among metal oxide based adsorbents, iron and aluminium hydroxides and oxides have been reported to be particularly effective for arsenic removal from water, including activated alumina and granular ferric hydroxide, approved as one of the best available technologies (BAT) [5,6]. Simultaneously, comparative studies showed that iron oxides exhibit higher sorption capacity toward As(V) (which is less influenced by the pH of the medium) than aluminium oxides, and also are much more effective adsorbents for removal of As(III) species [8]. Adsorption of As(III) and As(V) on the iron oxide surface occurs via a different mechanism, resulting in different optimal conditions and slower arsenite removal. Due to the high positive charge of the iron oxide surface below its pH$_{pzc}$, adsorption of arsenates occurs with the highest efficiency at acidic pH, while arsenites are adsorbed with better efficiency in neutral and alkaline environments. Therefore, the adsorption process of both arsenic species usually requires a preoxidation step [5,6]. Considering the high oxidation potential of MnO$_2$ for As(III), it is an effective additive for iron oxides, improving their adsorption performance toward arsenites in a wide pH range including acidic conditions. Simultaneously, a different mechanism of As(III) removal contributes to the development of new adsorption sites and higher sorption capacity of Fe–Mn binary metal oxide adsorbents [9–16].

Metal oxide based adsorbents are obtained in different sizes and shapes, in the form of nanoparticles, microparticles, granules, and nanocomposites exhibiting different porous characteristics which are crucial to their sorption properties. During the last two decades there has been observed significant progress in methods of synthesis of metal oxide adsorption materials. Among them the most widely studied are sol–gel processes, thermal decomposition and reduction, and hydrothermal synthesis [7]. Metal oxides, especially aluminium and iron oxides, are also constituents of industrial wastes including wastes from the processing of bauxites (red mud), fly ashes from combustion of coal and biomass, and water treatment residuals (WTRs) from drinking water production [4,17–20]. Since these waste materials are produced in great quantities and tend to be deposited, much effort has been made to develop suitable methods of their disposal including their utilization in environmental protection as catalysts, coagulation reagents and adsorbents for removal of heavy metals, selenates and arsenates from waters and wastewaters. Although trace amounts of heavy metals are present in all three discussed groups of wastes, standardized leachability and ecotoxicological tests confirm their suitability for adsorption processes conducted in the range of slightly acidic, neutral and slightly alkaline pH condition [21]. However, before use in adsorption processes, industrial waste materials, particularly bauxite residuals, require chemical pretreatment in order to ensure environmental safety.

Among the above-mentioned three groups of wastes, WTRs are the most promising, since they are not classified as hazardous wastes, are obtained from processing of natural water, exhibit neutral pH, and show relatively high arsenic sorption capacity. WTRs can be classified into two categories: (a) post-coagulation residuals whose content depends on the coagulant used (introduction of Fe (II)/Fe(III) salts or Al(III) salts leads to obtaining wastes in which respectively iron oxides (Fe-WTRs) or aluminium oxides (Al-WTRs) predominate); and (b) residuals from deironing and demanganization of underground or infiltration waters (Fe/Mn-WTRs) in which the concentration of Fe(II) and Mn(II) usually exceeds recommended values. Deironing and demanganization processes often involve intensive aeration of water resulting in oxidation of Fe(II) to Fe(III) and Mn(II) to Mn(IV), their hydrolysis and precipitation in the form of hydroxides and oxides without the use of additional chemicals. The obtained solid, Fe/Mn-WTRs, due to the presence of MnO$_2$ may also exhibit oxidative reactivity and may contribute to enhancement of arsenic removal from water [4].

Multicomponent industrial wastes containing iron oxides, in particular bauxite or post-coagulation residuals, have been widely used for arsenic removal from water. In contrast, WTRs from deironing and demanganization processes in drinking water production, exhibiting natural and simple chemical composition dominated by iron and manganese oxides, in spite of their potential advantages have rarely been evaluated as raw material in the production of adsorbents for arsenic removal from water [22–24]. Moreover, the appropriate composition of infiltration water (Fe: Mn ratio) and the mechanisms of deironing and demanganization processes (higher rate of Fe(II) oxidation) allow to assume that the obtained as a by-product sludge – due to the high content and availability of MnO$_2$ – may exhibit the desired oxidative and sorptive properties toward both As(III) and As(V). The aim of the present study was to characterize the properties of WTRs obtained from aeration of infiltration water, from production of water for consumption purposes, and to evaluate its usefulness as an arsenite and arsenate adsorbent.

2. Materials and methods

2.1. Materials

WTRs were obtained from Water Treatment Plant "Na Grobli" in Wrocław, Poland. The sludge was washed with distilled water, dried for 72 h at 25 °C, grinded in a mortar, sieved using a 1 mm sieve to remove large particles and stored in a desiccator for further analysis and experiments. All chemicals were of analytical grade. The As(III) and As(V) stock solutions (1 mg As cm^{-3}) were prepared with sodium (meta)arsenite NaAsO$_2$ (Sigma–Aldrich, 99%) and disodium hydrogen arsenate Na$_2$HAsO$_4 \times 7$H$_2$O (Sigma–Aldrich, 98%), respectively. These solutions were subsequently diluted to the concentrations required in adsorption experiments. All solutions were prepared with deionized water (18.3 MΩ cm^{-1}; Barnstead, EASYpure RF).

2.2. Characterization of WTRs

The pH of residual solid was determined in 0.01 M KCl solution at a 1:10 WTRs:solution ratio, after 24 h of reaction. The total concentration of Fe, Al, Mn, P, As, Zn, Pb, Cu, Cd, Cr were determined by atomic absorption spectrometry with a graphite tube (AAS Avanta) or inductively coupled plasma atomic emission spectroscopy (ICP-AES Thermo Scientific) after microwave mineralization