Microporous and Mesoporous Materials 273 (2019) 133–141

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

As(V) sorption by different natural zeolite frameworks modified with Fe, Zr and FeZr

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ARTICLE INFO

Keywords:
Arsenic
Sorption
Clinoptilolite
Mordenite
Chabazite

ABSTRACT

The structural effect of Fe-, Zr- and FeZr-modified clinoptilolite-, mordenite- and chabazite-rich tuffs was examined on the As(V) sorption from aqueous solutions. Batch experiments were conducted considering the sorbent mass, contact time and pH. The most probable sites where Fe and Zr species could be located in the zeolite frameworks after the modification were described: Na^+ exchangeable sites in the 10-ring and 8-ring channels of clinoptilolite, and inside the 12-ring and 8-ring channels and 8-ring side pockets of mordenite; Na^+, K^+ and Ca^{2+} sites within the D6R cages and barrel-shape cavities of chabazite. As(V) sorption capacities of Zr-modified materials (0.062 ± 0.008 mg/g) were higher than the Fe-modified ones (0.031 ± 0.007 mg/g). Isotherm results were best adjusted to the Freundlich model; FeZr-modified materials presented the highest affinity for arsenic. Estimated free energy values from the Dubinin-Radushkevich isotherm model suggested an ion exchange process. Kinetic data were well described by the pseudo-second order and intraparticle diffusion models, thus the sorption rate could have been controlled by two steps, the transfer of arsenic through the channel systems and the chemical interactions. Based on data modeling for the pH effect, zeolitic materials showed an optimal sorption in the pH range from 2 to 6; the major arsenic species involved in the sorption process were $H_2AsO_4^-$ and $HAsO_4^{2-}$. The mechanism for As(V) removal by the FeZr-modified zeolites was through the formation of an inner sphere complex via ion exchange.

1. Introduction

Arsenic is a metalloid widely distributed throughout Earth's environment, mainly forming part of rocks, minerals and ores mostly as sulfides or metal arsenides and arsenates; and it is considered as a high health risk due to the elevated toxicity of its inorganic compounds [1]. This element is incorporated to aqueous systems, mainly by leaching from rocks but also by anthropogenic activities, the most important route of arsenic exposure is through oral intake of drinking water [2]. Around 200 million people worldwide, including Bangladesh, India, Nepal, China, U.S., Argentina, Chile, Peru, Canada, Mexico, Poland, Italy, Finland, Spain, among others, are exposed to water with arsenic concentrations exceeding 10 μg/L [2,3] which is the recommended guideline value of the WHO [1]. Long term arsenic-contaminated drinking water consumption has been associated to very serious health complications including dermatological, neurological, reproductive, respiratory, cardiovascular and hematological diseases [4,5].

In order to mitigate the adverse effects of arsenic ingestion, various methods as coagulation and electrocoagulation [6,7], reverse osmosis [8], microbial remediation [9], photocatalytic oxidation [10] and sorption [11] have been employed to remove this element from water. Among them, sorption is the most extensively used process as it does not require sophisticated instrumentation or complicated procedures and offers satisfactory results. Over the last decade, sorption on natural materials, local minerals and residual wastes has been investigated [12–14] as these materials are inexpensive and readily available to the As affected communities. The surface of these kinds of sorbents is usually modified to improve their low or null arsenic sorption capacities. Single and bimetallic surface modifications with iron, manganese, zirconium, cerium and cupper have been used for this purpose [15–18]; among them, an iron-impregnated biochar and a zirconium-iron-modified sand were effective for arsenic removal, due to their remarkable As selectivity [19,20].

Zeolites are easily available minerals widely used in water

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https://doi.org/10.1016/j.micromeso.2018.07.003
Received 15 March 2018; Received in revised form 4 June 2018; Accepted 2 July 2018
Available online 03 July 2018
1387-1811/

treatment. These materials are integrated by hydrated aluminosilicates and have a porous crystal structure characterized by channels and cages of defined sizes. Their pore systems are occupied by water, alkali and alkaline earth cations that provide molecular sieve properties and cation-exchange abilities [21]. The zeolites structures can greatly differ in size and shape depending not only on their structures, but also on their elemental compositions.

Although more than 50 types of natural zeolites have been identified around the world (China, Jordan, Japan, Turkey, northern Europe, U.S., Mexico, New Zealand, etc.) [22,23], just few investigations have reported their use as arsenic sorbent materials. Li et al. [24] employed a HDTMA-modified clinoptilolite-rich tuff and found a maximum sorption capacity of 7.2 mmolAs(V)/kg, while Chutia et al. [25] used the same modification on a clinoptilolite- and a mordenite-rich tuffs, and the maximum sorption capacities were 45.33 and 97.33 mmolAs(V)/kg; the differences among the sorption capacities could be attributed to the experimental conditions, but also to the zeolite structure and composition. Other modifications such as iron, manganese, iron-manganese and cerium-iron have been reported on clinoptilolite-rich tuffs for the removal of arsenic [16,26–28].

The nature and topology of the zeolite frameworks define their physical and chemical properties such as the Si/Al ratio, internal surface area, pore volume, void volume, cation exchange capacity, etc. [29], which are essential to the sorption process. Although the zeolite structure plays an important role over the modification, this aspect has not yet been studied for different zeolite frameworks for the As removal. The most mineable and commercial natural zeolite types are clinoptilolite, mordenite and chabazite [23]; these zeolites differ from each other on their structures and compositions, for instance, clinoptilolite forms a monoclinic crystal system, its unit cell formula is $(Na,K,Ca_{0.5},Mg_{0.5})_6$ $[Al_6Si_{30}O_{72}]\cdot 20H_2O$, and its exchange capacity is 2.16 meq/g; the Si/Al ratio of clinoptilolite varies from 4.0 to 5.8 when it comes from sedimentary rocks and its void volume fraction is around 0.34. Mordenite forms an orthorhombic crystal system whose unit cell formula is $(Na_2,Ca,K_2)_4$ $[Al_8Si_{40}O_{96}]\cdot 28H_2O$; its exchange capacity, Si/Al ratio and void volume fraction are: 2.29 meq/g, from 5.4 to 9.4, and 0.28, respectively. Finally, the rhombohedral crystal of chabazite is described by the unit cell formula $(Ca_{0.5},Na,K)_x$ $[Al_xSi_{12-x}O_{24}]\cdot 12H_2O$; its exchange capacity, Si/Al ratio and void volume fraction are: 3.84 meq/g, from 1.5 to 4.5, and 0.47, respectively [21,29–31].

Despite the fact that researches have been focused on the effectiveness of zeolites modifications, there is little information available in the literature about the decisive role of the structure of the different zeolites over the surface modification and thus the arsenic sorption behavior. Therefore, the aim of the present work was to compare the As (V) sorption behavior of three different zeolite frameworks, clinoptilolite, mordenite and chabazite, considering the effect of iron and zirconium modifications (mono and bimetallic modifications: Fe, Zr and FeZr) and the influence of different experimental parameters, such as the mass of sorbent, contact time and pH.

2. Materials and methods

2.1. Natural zeolitic sorbents modifications

Clinoptilolite-, mordenite- and chabazite-rich tuffs (ZC, ZM and ZCH, respectively) were collected from different Mexican deposits, in the States of Oaxaca, Tamaulipas and Sonora, respectively; they were crushed and sieved into a particle size fraction between 0.42 and 0.84 mm. Modified sorbents were achieved according to a previous work [32]. Natural zeolites, ZC, ZM and ZCH, were firstly sodium exchanged by a refluxing process: natural zeolites were put under reflux with 0.2 M NaCl solution during 3 h in a zeolite:solution ratio of 1:10, once time was completed, the NaCl solution was changed and the procedure was repeated. After sodium modification of ZC, ZM and ZCH, samples were washed with purified water until no presence of chloride was detected through the $AgNO_3$ test, these materials were dried at 60 °C and labeled as Na-ZC, Na-ZM and Na-ZCH, respectively.

Subsequently, the sodium-modified materials (Na-ZC, Na-ZM and Na-ZCH) were treated using 0.1 M $FeCl_3$ or 0.1 M $ZrOCl_2$ solutions in a similar way as for the sodium modification; after the Fe or Zr treatments were completed, samples were washed and dried as above, these samples were labeled as Fe-ZC, Zr-ZC, Fe-ZM, Zr-ZM, Fe-ZCH and Zr-ZCH. Finally, bimetallic sorbents were obtained also by refluxing using a 0.1 M $FeCl_3$ and 0.1 M $ZrOCl_2$ solution through the same conditions as above. Finally, zeolitic materials were washed with purified water and dried; iron-zirconium-modified materials were labeled as FeZr-ZC, FeZr-ZM and FeZr-ZCH.

2.2. Complementary characterization

Natural, sodium-exchanged, iron-, zirconium- and iron-zirconium-modified zeolitic materials were previously characterized by different techniques including scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS), X-ray powder diffraction (XRD), Fourier transform-infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). Results from the above techniques, the pH of the point of zero charge (pH_{PZC}) and the textural properties of the materials by BET analyses were reported elsewhere [32].

Clear different morphologies among the zeolite-rich tuffs were observed by SEM which were in accordance with the main crystalline phases identified in each sample by DRX; characteristic coffin shaped crystals, intertwined thin fibers and cube-like rhombohedral crystals were observed for clinoptilolite-, mordenite- and chabazite-rich tuffs, respectively; it is worth mentioning that no significant changes in the X-ray diffraction patterns were observed after treatments. Based on the EDS analyses, it was possible to identify the following elemental changes: after sodium treatment, it was observed a drastic increment of Na content in ZCH (192%) compared to ZC (12%) and ZM (11%); and by the iron and zirconium treatments, the incorporated sodium content decreased for the three zeolitic samples. Additionally, for ZCH, it was observed a potassium decrease after the Fe and Zr modifications and a calcium reduction content after Fe treatments. The overall iron amounts were higher than the zirconium ones; the iron and zirconium preferences of the zeolite-rich tuffs were ZCH > ZM ≈ ZC and ZCH ≈ ZM > ZC, respectively.

Regarding XPS analyses, the predominant Fe and Zr species found on the zeolitic surfaces were FeOOH, Fe_2O_3 and $Zr(OH)_4$, which were in good agreement with the results found by IR spectra of FeZr-modified zeolitic materials; these results agree with those reported by Chmielewská et al. [33] who fully described the presence of FeOOH species mainly located outside of a clinoptilolite zeolite framework after iron modification, and according to Brown et al. [34], it is likely to find zirconium hydroxides species in aqueous solutions and on solids materials. The presence of these chemical species on the zeolite-rich tuffs induced an increment of the specific surface areas and a reduction of the mean pore diameters. ZC and ZM presented the most notable changes after FeZr modification as their specific surface areas increased 8.7 and 3.8 times, and their pore diameters were reduced 75 and 49%, respectively. The surface area of ZCH increased only 1.2 times and its mean pore diameter remained relatively constant around 3.8 nm, however, FeZr-ZCH presented the highest surface area (339.4 m^2/g). Finally, the point of zero charge (pH_{PZC}) for the Na-modified zeolite-rich tuffs changed after the bimetallic modifications (from 5.1, 8.1 and 4.9 to 2.2, 2.5 and 3.0 for FeZr-ZC, FeZr-ZM and FeZr-ZCH, respectively).

Additionally to the aforementioned characterization, it was determined the cation exchange capacities (CEC) and the external cation exchange capacities (ECEC) of the Na-ZC, Na-ZM and Na-ZCH; it was also analyzed the Na, Fe and Zr content of the Na-, Fe-, Zr- and FeZr-modified materials by neutron activation analysis.

Determination of the cation exchange capacity (CEC) was conducted