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Unexpected Precipitation Observed during Arsenic Removal from Water via Sorbent Modified with a Mixed Oxidation State Manganese

Andrey E. Krauklis^{1,2*}¹Department of Mechanical and Industrial Engineering, Norwegian University of Science and Technology, 7491 Trondheim, Norway²Department of Environmental Science, University of Latvia, Riga, LV-1004, Latvia

*Corresponding author: Andrey E. Krauklis, Department of Mechanical and Industrial Engineering, Norwegian University of Science and Technology, 7491 Trondheim, Norway, Tel: +37126810288; E-mail: andrejs.krauklis@ntnu.no

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Abstract

Drinking water contamination with As(V) is a crucial problem for millions of people dependent on groundwater resources in some regions of the world. Accumulation of arsenic compounds in the body by using such water poses serious health risks. Among many types of materials, Mn-modified sorbents are used for water treatment and arsenic removal. In this short communication, a newly observed phenomenon is reported, being an unexpected precipitation process occurring during the As(V) sorption from an aqueous solution via Mn-modified clinoptilolite. The quantity of formed precipitates was observed to increase with the initial concentration of As(V) present in water. While this short communication is intended only to report a novel observation, some implications can be expected. Additional studies are required to understand the underlying mechanism and implications of such precipitation during the water treatment process, raising questions on limitations of the use of such sorbents. While it is not completely certain, limited experimental evidence indicates that precipitates are formed by interaction of $Mn_8O_{10}Cl_3$ (mixed oxidation state Mn) and As(V), and exist in the form of hydrates. The precipitates are unstable in air at room temperature and moderate humidity, and degrade shortly thereafter outside of water solution.

Keywords: Water treatment; Precipitation; As(V); Arsenic removal; Sorption; Manganese

significant health risks and may lead to arsenicosis [3]. Arsenic contamination is both natural and due to human activity. Weathering of rocks and minerals is a typical example of a natural process, while metal waste, fertilizers, fossil fuel combustion and pesticides are due to agricultural and industrial activities [4-6].

Sorption is considered as one of the most feasible water treatment techniques in arsenic removal because of its relatively low costs [7-10]. Zeolites are highly crystalline, microporous and hydrated aluminosilicate minerals, which contain alkali or alkaline cations. Clinoptilolite is a high SiO_2 content heulandite group mineral and often is the main component of natural zeolites. Unmodified zeolites usually have a low affinity for arsenic due to an electrostatic repulsion between the anions and the framework of the zeolite. In such cases, surface modification, i.e. via manganese compounds, is a possible route for substantially improving oxyanion sorption [9].

Manganese compounds are used for modification of sorbents for As(V) removal from water [11,12]. Clinoptilolite modification with manganese oxides significantly enhances sorption capacity of As(V) compared to an unmodified clinoptilolite [11-13]. $Mn_8O_{10}Cl_3$ -modification improves As(V) sorption capacities of zeolites [11,12]. As(V) has affinity towards crystalline $Mn_8O_{10}Cl_3$ [11]. Thus, the newly observed phenomenon is important to understand and consider when Mn-modified sorbents are to be used in practice.

During sorption experiments of a mixed oxidation state Mn-modified natural zeolites (clinoptilolite) for removal of As(V) in water, an unexpected precipitation was observed, in result of which translucent greyish flakes were formed and sedimented.

The aim of this short communication is to report the newly observed phenomenon, which is of significance for the removal of arsenic compounds from water using manganese-modified sorbents. This phenomenon has not been reported before to the best knowledge of the author.

Introduction

Groundwater contamination with As(V) compounds is a problem for millions of people as these resources are crucial for use as drinking water [1-3]. Accumulation of arsenic compounds in the body due to use of such water poses

Materials

Clinoptilolite-rich (clinoptilolitic content 86–94%) natural zeolite from Slovakian deposit Nižný Hrabovec was modified with a mixed oxidation state manganese compound $\text{Mn}_8\text{O}_{10}\text{Cl}_3$ and was then used as a sorbent for arsenic removal. The specific weight of the unmodified material was 2200–2440 kg/m^3 and porosity was 24–32%. The material also contains cristobalite, clay mica, plagioclase, rutile, quartz. Size of particles was 1–2.5 mm [12,14].

The modification method of natural zeolites with a mixed oxidation state manganese oxide used in this communication is also reported in two other works [11,12]. Conditions of the modification are also consistent with that of $\text{Mn}_8\text{O}_{10}\text{Cl}_3$ synthesis described by G. Buisson [15]. 100 g of raw material were weighted and dried in air atmosphere in the oven for 1 h at 70°C. 2.5 M MnCl_2 and 10 M NaOH solutions were prepared. While mixing, 100 mL of 2.5 M MnCl_2 solution were added to the zeolite. Then, 1 mL of 10 M NaOH solution was added. The mixture was stirred and then aged for 24 h. After, it was placed in the oven for 3 h at 150°C, resulting in the densified modified zeolite mass. This mass was then placed in the muffle furnace and was held there for 5 h in air atmosphere at 550°C. After, it was taken out and cooled down in air at room temperature. After cooling, modified zeolite was washed with 300 mL of DI water. Material was dried in air for 1 h at room temperature, and further dried in the oven Gallenkamp Plus II (London, UK) for 4 h at 60°C. Modified material had Mn content of 8.40 ± 0.51 w%.

Unmodified natural clinoptilolite is able to sorb up to 0.36 \pm 0.02 mg/g of As(V). Mn-modification increases sorbed amount of As(V) up to 13.7 times (4.92 ± 0.30 mg/g) [11]. The amount of Mn compound was the same in all the studied samples.

All compounds used during this work were of analytical grade ($\geq 98\%$). Sodium hydroxide was obtained from Sigma-Aldrich (Riedel-de Haën, Germany). Manganese(II) chloride tetrahydrate was obtained from Firma Chempur (Piekary Śląskie, Poland). All aqueous solutions were prepared using high purity deionized water (10 – 15 $\text{M}\Omega\cdot\text{cm}$), produced via water purification system Millipore Elix 3 (Billerica, USA). Arsenate solutions were prepared using disodium hydrogenarsenate heptahydrate $\text{Na}_2\text{HAsO}_4\cdot 7\text{H}_2\text{O}$ obtained from Alfa Aesar (Haverhill, USA).

Experimental

SEM, EDX and XRD

Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) were performed using PhenomWorld Phenom ProX (Waltham, USA) in backscattered electron regime with working voltage of 15 kV. Studied material was covered with a thin layer of gold in order to prevent charging due to electron beam. Gold sputtering was performed using Quorum Technologies Emitech K550X (Laughton, UK).

X-ray diffraction (XRD) was performed using instrument Bruker D8 Advance (Billerica, USA). Radiation source: $\text{Cu K}\alpha$, $\lambda = 1.54180$ Å; Anode voltage 40 kV; Anode current 40 mA; $\text{K}\beta$ filter 0.02 mm thick nickel foil; slits: divergence 0.6 mm, anti-scattering 8.0 mm; scanning range: $2\theta=3\text{--}55^\circ$, step 0.02° , step time 0.5 s; energy-dispersive one-dimensional detector Lynx Eye.

A combination of SEM, EDX and XRD allowed to ensure that the zeolite was successfully modified with a crystalline mixed oxidation state manganese oxide-chloride $\text{Mn}_8\text{O}_{10}\text{Cl}_3$. The details of these results are reported in another work [11].

Arsenic removal experiments

Arsenic removal or sorption experiments were conducted using a batch system. $\text{Na}_2\text{HAsO}_4\cdot 7\text{H}_2\text{O}$ was used for preparation of arsenic solutions of various concentrations (5, 10, 25, 50, 100, 200 and 300 mg/L). 0.5000 ± 0.0001 g sorbent was weighed in each glass vessel using analytical scales Kern ALJ 220-4 (Balingen, Germany) and 30.00 ± 0.05 mL As(V) solution was then added to every vessel. Vessels were shaken for 24 h at room temperature ($23 \pm 1^\circ\text{C}$) at 150 rpm using orbital shaker Biosan Multi-functional Orbital Shaker PSU-20i (Riga, Latvia) to ensure sorption equilibrium was achieved.

Results and Discussion

EDX analysis of the modified sorbent indicated that it contained 8.40 ± 0.51 w% of the Mn. EDX of the initial zeolite showed it contained no traceable amounts of Mn.

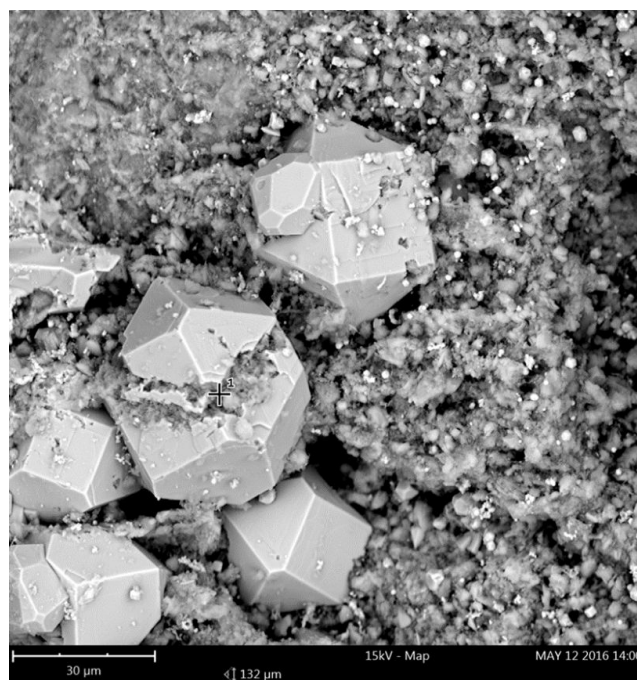


Figure 1: SEM micrograph of a crystalline $\text{Mn}_8\text{O}_{10}\text{Cl}_3$ on the surface of the clinoptilolite (resolution given by the microscope manufacturer ≤ 14 nm).

XRD diffraction patterns showed that the sorbent was modified with a new crystalline phase, which was found to be $\text{Mn}_8\text{O}_{10}\text{Cl}_3$ [11,12].

SEM micrograph of the crystalline $\text{Mn}_8\text{O}_{10}\text{Cl}_3$ modification compound on the surface of the zeolite is shown in **Figure 1**. The sorbent is also characterized and described in more detail in another works [11,12].

During the arsenic removal (sorption) experiments from water using a mixed oxidation state Mn-modified natural zeolites (clinoptilolite) a sudden unexpected precipitation was observed, in result of which translucent greyish flakes were formed and sedimented as shown in **Figure 2**.



Figure 2: Greyish precipitates formed during water treatment for As(V) removal using mixed oxidation state manganese compound $\text{Mn}_8\text{O}_{10}\text{Cl}_3$ -modified clinoptilolite zeolite.

This phenomenon has not been reported before to the best knowledge of the author. This is of significance and might have implications for the removal of arsenic compounds from water using manganese-modified sorbents. Furthermore, the quantity of formed precipitates was observed to increase with the initial concentration of As(V) present in water (from 5 to 300 mg/L, studied in this work).

Limited experimental evidence indicates that precipitates are formed by interaction of $\text{Mn}_8\text{O}_{10}\text{Cl}_3$ (mixed oxidation state Mn compound) and As(V), and exist in the form of hydrates, since the precipitates are unstable in air at room temperature and moderate humidity, and degrade in air fairly quickly.

While this short communication is intended only to report a novel observation, some implications can be expected. Additional studies are required to understand the underlying mechanism and implications of such precipitation during the water treatment process with Mn-modified sorbents, raising questions on limitations of the use of such sorbents.

A possible explanation is a complexation between the zeolite-modifying compound of a mixed oxidation state $\text{Mn}_8\text{O}_{10}\text{Cl}_3$ and As(V) in water with the resulting products partially precipitating. The product is likely in a form of hydrates. This mechanism is speculated by analogy with Fe-modified sorbents that are often used in arsenic removal

[11,12,16,17], which form inner sphere complexes. Out of 9 mg of As(V) that were present in the 300 mg/L initial solution, only 0.18 mg could be uptaken by the unmodified zeolite, while the modified sorbent was able to adsorb 2.46 mg As(V). The difference (2.28 mg) was likely uptaken by the modification compound $\text{Mn}_8\text{O}_{10}\text{Cl}_3$ itself. While speculated, this difference, possibly partially, was likely involved in the complexation.

Conclusion

In this short communication, a newly observed phenomenon was reported, being an unexpected precipitation process that occurred during the As(V) sorption from an aqueous solution via Mn-modified clinoptilolite. Furthermore, with an increasing concentration of As(V) in to-be-treated water samples, the amount of formed precipitates increased proportionally. Precipitates are likely formed by interaction of $\text{Mn}_8\text{O}_{10}\text{Cl}_3$ (mixed oxidation state Mn) and As(V), possibly via complexation. The precipitates had a hydrated nature and were unstable in air even at room temperature and moderate humidity, and degraded quickly outside of water solution. The concentration of As(V) in water decreased during the arsenic removal experiment indicating that part of As(V) was sorbed and was likely involved in formation of these precipitates, which was indicated by the proportionality of quantity of formed precipitates and the initial concentration of As(V) present in water solutions. While this short communication is intended only to report a novel observation, some implications can be expected. Additional studies are required to understand the underlying mechanism and implications of such precipitation during the water treatment process, raising questions on limitations of the use of such sorbents.

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