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Original Research

Removal of As (III) and Cr (III) on Modified Clinoptylolite

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Abstract

We investigated the removal of As(III) and Cr(III) on the zeolite modified with manganese oxides. The results of our research show that zeolite behaves as a heterogeneous catalyst and removal of investigated elements occurs due to their oxidation and adsorption, as well as precipitation. This paper investigates the process with respect to the zeta potential and the size of Cr and As hydroxo complex particles at different pH.

Keywords: As removal, Cr removal, sorption, clinoptylolite modified with Mn

Introduction

Arsenic is a toxic trace element widely present in the environment. Its predominant forms include oxyacids of As(V) or arsenates, and oxyacids of As(III) or arsenates (III) [1]. Excessive concentrations of arsenic have been found locally in underground waters [2]. Due to arsenic toxicity, WHO has set its highest acceptable concentration in potable water at 10 μg/L (10 ppb). Arsenic in water and wastewater occurs mainly as arsenates As(V) and more toxic arsenates As(III). It forms organic and – highly toxic – inorganic (highly toxic) compounds. Its natural concentration in soil does not exceed 10 mg/kg. [3].

Arsenic in wastewaters may originate from various industrial plants, where its compounds are used in production of numerous products. In natural conditions, As(V) is reduced to As(III) by organic substances and bacteria and as such As(III) has been found in anoxic deposits; however, opposite reactions, oxidation of As(III) to As(V), are also possible. The highest acceptable arsenic concentration in potable water has been set at 10 μg/L in many countries.

Hardly soluble arsenic compounds are precipitated with whitewash (calcium arsenate and arsenite). Such an apparently cheap method of chemical precipitation is not a convenient option as it produces a lot of toxic deposits. More popular methods employ adsorption on activated carbon as well as on manganese and iron ores [4-6]. Adsorption of As(V) on MnO_2 minerals has already been observed by Manning et al. [7] and Radu et al. [8]. However, adsorption of As(III) on manganese oxides consisting predominantly of Mn (IV) has not been observed yet, as reported by Amirbaham et. al. [9]. Roberts et al. reported that the addition of ferrous leads to better arsenic removal efficiency than the addition of ferric. It is reported that mechanisms for arsenic removal include adsorption onto the hydroxide surfaces, and electrostatic attraction between magnetite and $HAsO_4$ or H_2AsO_4 [10, 11].

Chromium is a major pollutant known to be carcinogenic and mutagenic. In the environment, chromium compounds have mostly two oxidation states, namely Cr(VI) and Cr(III). Hexavalent chromium, frequently found in wastewaters from the production of stainless steel, tanned leather, dyes, and pigments [12, 13], is highly toxic to living organisms, whereas Cr(III) is essential for maintaining glucose, lipid, and protein metabolism in mammals [14, 15]. Chromium(VI) can be reduced to Cr(III) by natural reductants such as

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organic matters [12, 16-18]. However, Cr(III) can again be oxidized to Cr(VI), making the potential threat of chromium(III)? a serious environmental concern [19]. The maximum Cr(VI) concentration in potable water is 20 μg/L. The following methods can be considered for Cr(VI) removal from water and wastewater: chemical reduction of Cr(VI) to Cr(III) with $NaHSO_3$, Fe(II) compounds and other reductants [20-21], sorption [23, 24], membrane filtration Alliane et al. [25], or by dried activated sludge biomass [16]. Chromium(III) can be oxidized to Cr(VI) by manganese oxide minerals [12] and synthetic δ-MnO_2. The Cr(III) oxidation rate depends on the initial concentration of manganese oxide, solution acidity, and existing Cr(III) species [26, 27].

The main objective of the study was to investigate and evaluate a mechanism of As and Cr removal on H-zeolite and Mn-zeolite.

Methods and Materials

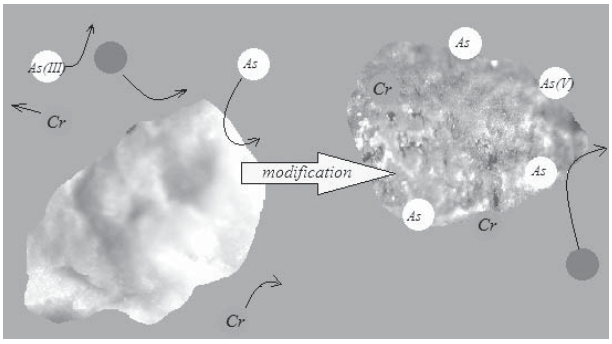
The metals were determined with Spectr AA 20 plus, manufactured by Varian, and Solar S4, manufactured by Thermo Jarrell Franklin, USA. Trace amounts of metals were determined by the GTF graphite cell method using samples of magnesium nitrate(V) and palladium nitrate(V) as modifiers. The analyses conform to the standards (PN-EN ISO11969, 1999 and PN-EN 1233, 2000) [28, 29].

– As determination: atomic absorption spectroscopy with atomization in a nitrous oxide-acetylene flame using the hydride technique (PN-EN ISO 11969); the analyses were done at a wavelength of 193.7 nm and slit width of 0.5 nm
– Cr(III), Cr(VI) determination: atomic absorption spectroscopy with atomization in a nitrous oxide-acetylene flame (PN-EN ISO 1233); the analyses were done at a wavelength of 357.9 nm and slit width of 0.5 nm.

Qualitative analyses were carried out on filtered solutions. The sorption process was studied under static conditions, at pH ranging from 2 to 12.5. A contact time of 120 minutes was assumed based on previous reports, when the adsorption equilibrium was investigated. The amount of the dosed zeolite was constant at 15 g/L. Solutions of 100 mg/L were used in the experiments, prepared from a distilled water and the Merck reference standards (chromium(III) nitrate(V) and arsenic(III) oxide, dissolved in 0.1 mole/L HNO_3), with the concentration of 1000 mg/L of each of the ions, As(III) and Cr(III).

The relationship between electrokinetic potential and the size of metal hydroxo complex agglomerates vs. solution pH was determined with a zetameter, manufactured by Brookhaven, using a phase analysis of dispersed laser light in a dispersed medium. The method enables us to measure individual particles with diameters ranging from 30 nm to 30 μm. A 100 mg/L solution of the ions was prepared with distilled water; the solution's pH was adjusted with 0.1 mole/L NaOH and HCl. The solution was stirred for 3 minutes and then its electrokinetic potential and particle size were determined.

Natural zeolite (clinoptilolite) from Hungarian deposits was used in the experiment. The zeolite consisted of: clinoptilolite (55%), ash and volcanic glass (26%), quartz (6%), and montmorillonite (13%). Its density was 2.4 g/cm^3 and its bulk density (ground material) 0.69g/cm^3. The mineral porosity of zeolite was 30-50% while the ion-exchange capacity was 1.15 mvalMe/g [17], and diameter was 1 mm. The mineral was washed with hydrochloric acid and distilled water and subsequently dried at 105ºC (zelite H) and modified with Mn ions (Zeolite Mn). Zeolite Mn, referred to as "Diapar," was obtained by the original method patented by the authors [30]. Zeolite H contains high, concentrations of silicon compounds (320 mg/g), aluminum (60 mg/g), and alkaline earth metals (sodium, calcium, iron, and magnesium), whereas zeolite Mn contains fewer silicon compounds (290 mg/g) and aluminium (53 mg/g) relative to the total mass, which results from introducing manganese ions to zeolite, owing to which its concentration is quite high (78 mg/g) [19, 20]. Evaluation of the zeolites by infrared spectra analysis showed [2] that the zeolite Mn has better catalytic properties than non-modified zeolite. The active manganese dioxide deposited on the surface is highly complex. It forms various polymorphic types, considerably deviating from the stoichiometric formula, and therefore shows catalytic and sorptive properties. Zeolite Mn is black with a metallic sheen (Fig. 1).



Scheme 1. Modification of zeolites.

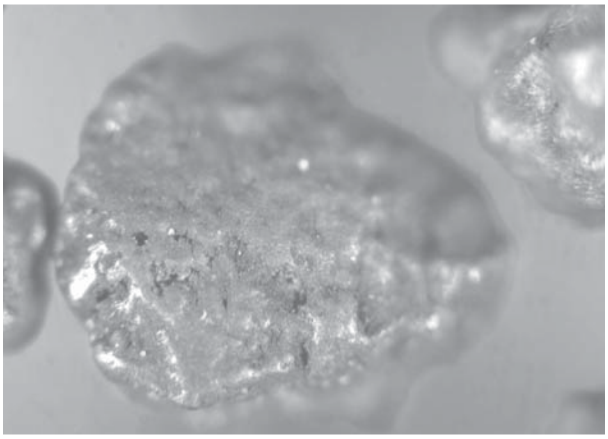


Fig. 1. Microscopic picture of zeolite Mn.

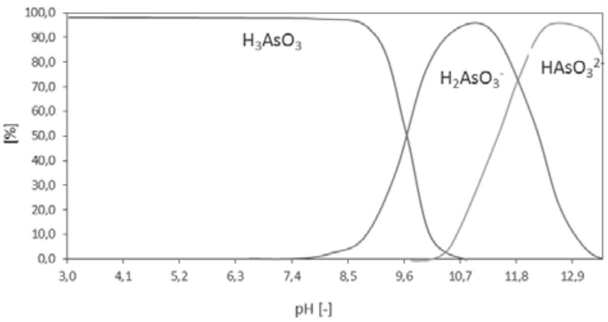


Fig. 2. The presence of As(III) complexes in aqueous solutions as a function of their pH.

Results and Discussion

Arsenic (As) Adsorption

In acidic and neutral environments, arsenic(III) forms undissociated orthoarsenous acid H_3AsO_3 (Fig. 2). The As^{3+} cation occurs only in strongly acidic environments. At such a high concentration of protons, arsine AsH_3 can also be formed, which is a strong reducing agent, volatile and highly toxic, with its boiling point at -62.5ºC. In an alkaline environment, arsenic(III) is present as negative hydroxo complexes (Fig. 2), which form real solutions even at concentrations of 100 mg/L. Such a phenomenon is a result of the absence of electropositive hydroxo complexes that self-coagulate with negative complexes. This is why the solution used in the study was transparent even at high concentrations, and it was impossible to measure the size of arsenic hydroxo complexes or their zeta potential with a zeta-meter (which detects particles with diameters >30 nm).

The results presented in Fig. 3 show that about 1.8% of As(III) remains on the filter. About 5.4% of arsenic ions from the filtered solution adsorbs on H-zeolite. The removal rate on Mn-zeolite was much higher; it was about 11-12% and reached 14% when pH increased to 10.4. The As(III) removal rate on H-zeolite within the pH range from 11.2 to 12 is nearly the same as on a filter. Therefore, it may be concluded that As ions are not adsorbed on H-zeolite in a strongly alkaline environment. Moreover, much lower adsorption was observed on Mn-zeolite (the removal rate dropped to 3.7%). An analysis of the results showed that arsenic adsorption on H-zeolite was accompanied by an increase of hydrogen ion concentration in the solution due to proton release from H-zeolite, where they were introduced during modification with hydrochloric acid. The nature of the chemical environment is also changed during sorption on Mn-zeolite (Fig. 3). For example, at the initial range of pH_0 from 8.0 to 10.4, where the As(III) removal rate is the highest, pH_e value decreases to 5.8-7.0 (Figs. 3 and 4). In the alkaline environment the equilibrium moves to the right because the released hydrogen ions are bound by hydroxide ions. Also, at higher pH the anions of higher valency predominate, which are repelled by negatively charged adsorbent surface.

The catalytic properties of manganese-modified zeolite in the presence of As(III) have been examined by Anielak et al. [31]. They showed that the redox potential decreased rapidly at pH ranging from 4 to 9, and arsenic solution showed buffer properties in the presence of Mn zeolite (1 mg As(III)/10g of Mn zeolite). A solution in equilibrium with the adsorption process at the initial pH_0 of 4-9 has a stable final pH value ($pH_e = 4$) resulting from the redox reaction:

$$H_3As^{III}O_3+H_2O=H_3As^{V}O_4+2H^{+}+2e \qquad (1)$$

Protons released in the reaction reduce the pH value to 4. Catalytic properties of Mn zeolite in an acidic environment at pH<4 and in an alkaline environment at pH>9 are very weak or nonexistent.

The results presented in Fig. 3 confirm the above relationships. The lowest efficiency of As(III) removal on Mn zeolite is achieved at pH<4 and in strongly alkaline environments.

As surface of Mn zeolite gets hydrated in water and manganese dioxide is partly hydrated, As(III) becomes oxidized to As(V) with concurrent reduction of Mn(IV) to Mn(II) and proton release to the solution. In groundwater with excessive amounts of Mn(II) further reduction of Mn(III) to Mn(II) occurs, but at the same time Mn(II) is oxidized to Mn(III) and the equilibrium state is achieved between those two forms. The reactions and mechanisms of the process have been presented by Anielak [30] and can be presented in a general manner:

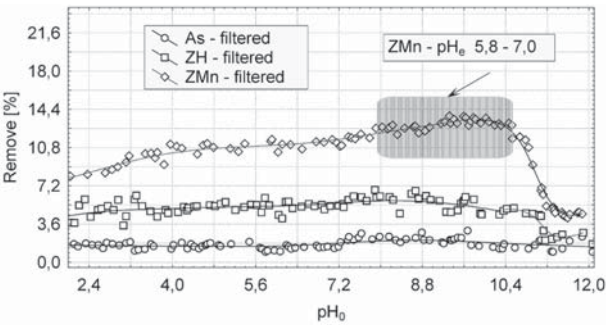


Fig. 3. As (III) sorption vs. pH_0 (initial) on zeolite modified with Mn and H. Zeolite dose 15g/100 mg of As(III).

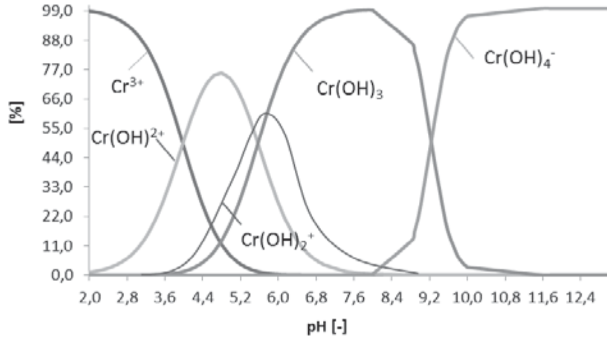


Fig. 4. Final pH (pH_e) vs. initial pH (pH_0) after the sorption process.

$$2Mn^{IV}O(OH)_2 + H_3As^{III}O_3 = 2Mn^{III}OOH + H_3As^{V}O_4 + H_2O \tag{2}$$

$$2Mn^{III}OOH + H_3As^{V}O_4 = Mn_2^{III}O(OOH)_2As(OH)_3 \tag{3}$$

As a result, the sorptive capacity of a zeolite surface increases as well as its catalytic activity. Zeolite does not require regeneration [32-34].

Cr(III) Adsorption

Chromium(III) forms positive or negative hydroxo complexes, depending on the pH of its aqueous solution (Fig. 5). Hence it should be concluded that its affinity to the electronegative surface of H-zeolite and Mn-zeolite will depend on the pH of the sorbate solution.

The measurement of the zeta potential and the size of particles formed in solution as a result of agglomeration of chromium hydroxo complexes are shown in Fig. 6.

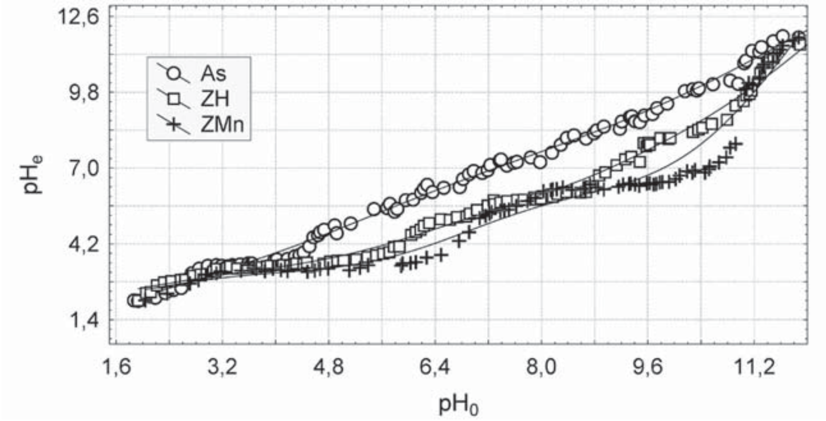


Fig. 5. The presence of Cr(III) complexes in aqueous solutions as a function of their pH.

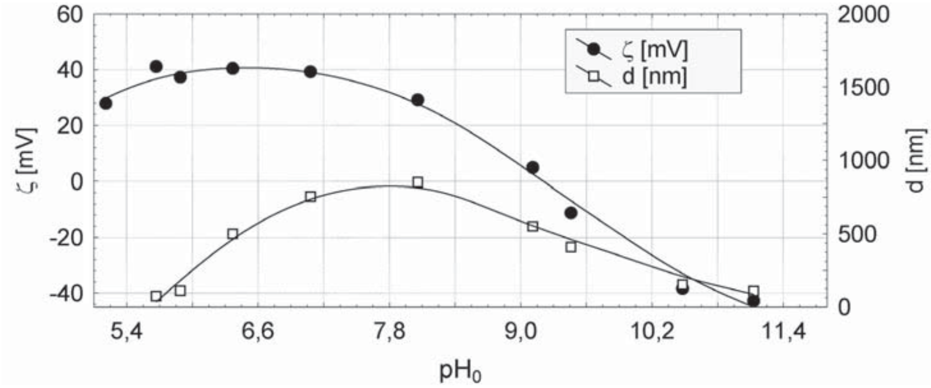


Fig. 6. The zeta potential and the size of hydroxo complex particles of Cr(III) (100 mg Cr^{3+}/L).

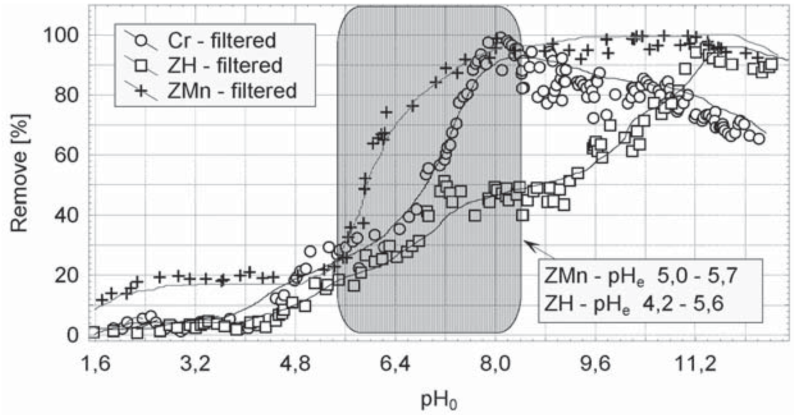


Fig. 7. The effect of pH_0 on removal of Cr(III) ions by sorption. D_z = 15 g/100 mg Cr(III).

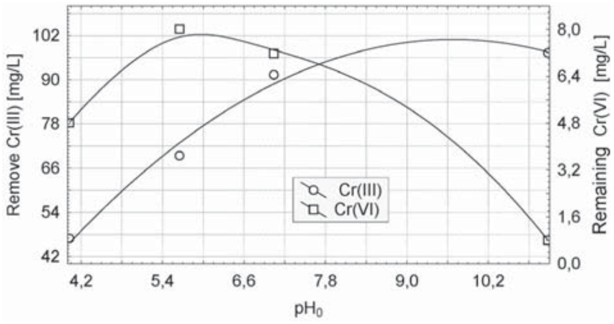


Fig. 8. Cr(III) removal on Mn zeolite and the concentration of the remaining chromium (VI) in the filtrate as a function of initial pH_0.

Measurements of the particle sizes and the zeta potential were possible within the pH range from 5.3 to 11.0. The solution at pH<5.3 was transparent, with hydroxo complexes of $Cr(OH)_2^+$, $Cr(OH)^{2+}$, and ions Cr^{3+} (which form aqua complexes) – Fig. 5.

The quantitative equilibrium between soluble complexes $Cr(OH)^{2+}$ and Cr^{3+} ions exists at pH about 4, while at pH>6, $Cr(OH)_2^+$ and precipitable complexes of $Cr(OH)_3$ dominate. The highest zeta potential (+40 mV) is observed at pH of about 6; it decreases when a pH increases above 7.5. At pH>8, negative complexes of $Cr(OH)_4^-$ appear and they predominate at pH>9,2; at such pH electropositive, electronegative and neutral hydroxo complexes are present. The electrokinetic potential drops to 0 mV as the result of the electrostatic equilibrium between the two complexes. The greatest particle size of 850 nm is found at pH of about 8. With pH changes from 6 to 8, considerable self-coagulation takes place and the particles grow intensely from 250 to 850 nm. The relationships correlate with the hydroxo complexes that are formed within the pH range in question.

Sorption, which is not associated with complex precipitability, occurs at pH<5 and its rate is close to 20% (Fig. 6).

The efficiency, of adsorption on Mn zeolite grows with increase pH. At the same time, precipitability of hydroxo complexes increases and large amounts of Cr(III) remain on the filter. At pH>5, significant self-coagulation of hydroxo complexes takes place. The highest chromium ion removal efficiency has been achieved for pH>5.6. As the study has shown (Fig. 7), H zeolite hinders chromium removal over practically the entire pH range.

As a result of hydrogen ion release, pH decreases in the presence of H zeolite from the initial pH_0 value of 5.6-8.6 to the pH_e value of 4.2-5.6. The study has also shown that – as in case of As(III) removal – Mn zeolite catalyses oxidation of Cr(III) to Cr(VI).

Catalytic oxidation of Cr(III) to Cr(VI) occurs at pH_0 of about 4 and the concentration of Cr(VI) in the filtrate is close to 5 mg/L (Fig. 8). The figure shows that the highest overall Cr removal was achieved in an alkaline environment. The concentration of Cr(III) oxidized to Cr(VI) in the filtrate decreases for pH above 6. At the same time, the amount of removed Cr(III) increases. The redox reaction that occurs is facilitated by the catalytic effect of zeolite and can be described as follows:

$$\text{Zeolite} - 3Mn_2^{IV}O_2(OH)_4 + Cr_2O_4^{2-} = \\ \text{Zeolite} - 3Mn_2^{III}O_2(OH)_2 + 2CrO_4^{2-} + 2H_2O + 2H^+ \tag{4}$$

The catalytic oxidation runs concurrently with reduction of Mn(IV) to Mn(II). It may be concluded from Fig. 8 that Cr(III) removal is associated with adsorption/incorporation of Cr(VI) to the zeolite structure, as found in the previous studies [30, 31].

Conclusions

- Mn zeolite catalyses sorption of the ions under study, oxidizing As(III) to As(V) and Cr(III) to Cr(VI).
- The considerable sorptive capacity of Mn zeolite with respect to As(III) and Cr(III) ions indicates the possibility of using the material to purify industrial wastewater at considerable concentrations of tens of mg/L.
- The highest efficiency of As(III) ion removal is achieved at the pH range from 8.0 to 10.4, with pH_e reduced from 5.8 to 7.0.
- Effective removal of Cr(III) is achieved at pH>6 mainly as a result of precipitation of hydroxo complexes $Cr(OH)_3$ and $Cr(OH)_2^+$.
- Based on the measurement of the electrokinetic potential and the size of particles precipitated due to self-coagulation of hydroxo complexes, the conditions of Cr(III) and As(III) removal by precipitation and sorption can be determined.
- Self-coagulation of hydroxo complexes occurs at high concentrations of Cr(III). The diameter of particles formed in the process is below 1 mm. Their size and electrokinetic potential are associated with their form that occur within the pH range under examination.

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