



Mimetite precipitation on Pb-clinoptilolite: an effective approach for arsenate removal from water

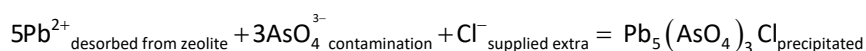
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Abstract

This short communication proposes a novel approach to arsenate remediation using *in situ* precipitation of mimetite [$\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$], a sparingly soluble mineral phase with an apatite structure. The Pb^{2+} source was provided by a lead-modified zeolite (clinoptilolite) loaded with approximately 70 g Pb/kg. It was reacted with arsenate (50 mg As/L) and chloride (20 mg Cl/L) at initial pH values of 2 and 7. Mimetite crystallized on and in the vicinity of zeolite due to the reaction of Pb(II) desorbed from zeolite with arsenate and chloride ions present in aqueous solution:



Mimetite formed rapidly resulting in efficient arsenate sequestration. At pH 7, arsenate removal reached 99.88% after 24 hr, with minimal lead release (<0.02 mg/L). These results demonstrate that lead-modified clinoptilolite is a promising material for a coupled sorption–precipitation mechanism which provides an effective strategy for arsenic immobilization in contaminated aqueous systems.

Keywords: Arsenic, Lead apatite, Zeolite, Water remediation, Sorption

1. Introduction

Arsenic is a ubiquitous and toxic metalloid present in the atmosphere, soils, rocks, natural waters, and living organisms. Its presence in drinking water poses a significant global health risk, with the World Health Organization (WHO) setting a guideline value of 10 $\mu\text{g/L}$. In natural waters, arsenic commonly occurs as inorganic oxyanions of trivalent arsenite [As(III)] under reducing conditions, or pentavalent arsenate [As(V)] under oxidizing conditions (Abdul et al., 2015; Smedley & Kinniburgh, 2002).

In many regions arsenic contamination of waters is a major environmental and public health crisis. Chronic exposure to arsenic contaminated drinking water has been linked to skin lesions, hyperkeratosis, melanosis, cancer (e.g. skin,

bladder, lung), peripheral neuropathy, gastrointestinal disorders, diabetes or cardiovascular disease. An estimated 140 million people worldwide are exposed to arsenic concentrations in drinking water that exceed the WHO guideline, particularly in South and Southeast Asia, parts of South America, and even regions of Europe and the United States (Murcott, 2012; Ravenscroft et al., 2011; World Health Organization, 2018). Elevated arsenic concentrations in major aquifers worldwide necessitate intensified research into the geochemical controls on arsenic distribution, mobilization mechanisms, and the development of efficient remediation strategies (Banning, 2021; Murcott, 2012; Smedley & Kinniburgh, 2002).

Arsenic removal from water typically relies on its immobilization via precipitation of low-solubility salts,

adsorption onto mineral surfaces, or ion exchange processes—principles that underpin most remediation technologies (Magalhães, 2002). However, existing methods such as coagulation-flocculation, activated alumina, and iron- or aluminum-based adsorbents face several limitations, including high operational costs, pH sensitivity or limited selectivity in the presence of competing ions (Sharma & Sohn, 2009). These challenges underscore the urgent need for alternative approaches that offer improved efficiency, long-term stability, and environmental safety.

In this short communication we explore a novel two-stage method for arsenic sequestration, combining adsorption and mineral precipitation. The approach involves the reaction of As(V)-bearing solutions with Pb^{2+} ions in the presence of Cl^- , facilitating the precipitation of mimetite, $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$, a sparingly soluble arsenate phase with an apatite structure. The Pb^{2+} source is provided by a lead-modified zeolite, where Pb^{2+} is sufficiently retained to prevent leaching in water but remains reactive in the presence of arsenate and chloride. The first stage involves the preparation of Pb-loaded zeolite, while the second stage focuses on its interaction with arsenic-contaminated solutions. The first results of laboratory experiments are presented, providing an evaluation of arsenic removal efficiency and an elucidation of the microscale mechanisms involved in mimetite precipitation. The results provide new insights into arsenate sequestration and demonstrate the potential of this method as an effective alternative to conventional treatment technologies.

2. Materials and Methods

2.1. Experimental materials

The experiments were conducted in polyethylene tubes at ambient laboratory temperature, which was approximately 25°C, without active temperature control. All solutions were prepared using double-distilled water and analytical-grade chemicals obtained from Thermo Scientific Inc. (Waltham, MA, USA) and Chempur Inc. (Piekary Śląskie, Poland). Sodium arsenate dibasic heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) was used as the source of arsenate ions, while lead nitrate ($\text{Pb}(\text{NO}_3)_2$) provided the lead ions. Chloride ions were introduced via sodium chloride (NaCl). The pH was adjusted dropwise using 0.5 M HNO_3 or 1 M NaOH, with the pH measured using a glass electrode and an ELMETRON (Zabrze, Poland) CPC-401 pH meter.

2.2. Zeolite modification by Pb-sorption

Zeolite rock, serving as the carrier of lead in the further experiments, was sourced from the Bystré deposit (Slovak Republic) and supplied by Zeocem, a.s. (Bystré, Slovakia). It was rich in clinoptilolite with identified admixtures of orthoclase, illite, and quartz. The material has been thoroughly characterized in previous studies (see, for example, Solińska & Bajda, 2022; Wołowicz et al., 2017, and the literature cited therein). Initially, in its calcium form, it was transformed into

sodium-exchanged clinoptilolite by reacting with a 2 M NaCl solution for 24 hr. The Na-modified clinoptilolite was then prepared for arsenate sequestration by first performing Pb^{2+} sorption, followed by thorough washing to remove excess Pb and desorb loosely bound ions, ensuring the zeolite was primed for subsequent arsenate interactions.

Aqueous Pb(II) solutions were prepared at concentrations of 100, 500, 1000, 2000, and 4000 mg Pb(II)/L with no pH adjustment. Sorption experiments were conducted in batch systems, where 40 mL of solution at varying Pb concentrations was mixed with 0.8 g of Na-transformed clinoptilolite. The slurries were shaken at room temperature for 24 hr. This was shown in previous studies to be sufficient for equilibrium between metal ions in solution and those sorbed on clinoptilolite (Bajda et al., 2004; Mozgawa & Bajda, 2005). Afterward, the samples were centrifuged at 4500 rpm for 10 min, filtered through 0.2- μm syringe filters, and analysed for Pb. Atomic Absorption Spectroscopy (AAS) was used to measure Pb concentrations in the solutions before and after the sorption experiments. The experiments were repeated in triplicate. The amount of Pb sorbed was calculated based on the difference between the initial measured and equilibrium concentrations. The sorption per 0.8 g of zeolite was calculated as: $(C_i - C_e) \times V$. To express sorption per kilogram of zeolite (mg/kg), this value was then divided by the zeolite mass (0.8 g) and multiplied by 1000, according to the equation: $(C_i - C_e) \times (V/m) \times 1000$. C_i was the initial measured concentration of Pb (mg/L), C_e was the equilibrium concentration (mg/L), V was the volume of solution in litres (0.04 L), and m was the mass of the zeolite in grams (0.8 g).

Pb-sorbed clinoptilolite resulting from the experiment at 4000 mg Pb/L was thoroughly washed with redistilled water and then centrifuged at 4500 rpm for 5 min. The Pb concentration in the solution resulting from the 7th washing cycle has dropped below the AAS detection limit (equal to 0.1 mg Pb/L). The solid was washed, air-dried, and subjected to acid digestion using 25 mL of hydrofluoric acid (HF), a few drops of perchloric acid (HClO_4), and 20 mL of hydrochloric acid (HCl) per 0.3849 g of zeolite. The digested samples were then analysed for total Pb content.

2.3. Arsenate sequestration by reaction with Pb-modified zeolite

To determine the equilibrium product of the reaction and define the reaction efficiency in terms of arsenate sequestration from solution, the Pb-modified zeolite, containing approximately 70 g of bound Pb per kg, was reacted with arsenate solutions (0.5 g of Pb-modified zeolite per 40 mL of solution containing 50 mg As(V)/L). The suspensions were shaken for 7 days in the presence of chloride ions (20 mg Cl/L) at pH 2 and 7. These two pH values were selected to represent contrasting conditions: pH 7 corresponds to near-neutral environments where mimetite is highly stable and exhibits minimal solubility, while pH 2 simulates acidic environments such as acid mine drainage, where mimetite stability is significantly

reduced and lead release from Pb-modified zeolite may occur (Bajda, 2010; Magalhães & Silva, 2003). The solution was sampled at 24 hr and 7 days and analysed for As (UV-Vis spectrophotometry) and Pb (AAS). Solid samples were collected after 1 week, washed three times with water, centrifuged at 4500 rpm, air-dried, and analysed using X-ray powder diffraction (XPRD) and scanning electron microscope with an energy dispersive spectrometer (SEM-EDS).

2.4. Analytical methods

Concentrations of As(V) in solutions were measured by spectrophotometry (Lenoble et al., 2003) using the molybdenum blue method, with a detection limit of 20 µg As(V)/L, on a HITACHI U-800 UV-Vis spectrophotometer at 870 nm. Pb concentrations were determined by atomic absorption spectroscopy (AAS) using a Savant AA spectrometer (GBC Scientific Equipment (Melbourne, Australia); detection limit: 0.1 mg Pb/L, $\lambda = 217$ nm).

Previously ground in an agate mortar, solid samples were analysed by XPRD using a Rigaku SmartLab diffractometer (2–72° 2 θ , step size 0.02°, 1 s/step). Phases were identified with the PDF-2 JCPDS database and XRAYAN software (KOMAR, Warsaw, Poland; Marciniak et al., 2006). The morphology and elemental composition of the solids were characterized using a

FE-SEM, Quanta 200 FEG, FEI Company, now part of Thermo Fisher Scientific, Hillsboro, OR, USA equipped with EDS. Air-dried powders and crystals were mounted on adhesive tape and imaged under low vacuum without any coating.

3. Results and Discussion

3.1. Zeolite modification by Pb-sorption

The results of lead immobilization, expressed as a function of initial and equilibrium Pb(II) concentrations, are presented in Figure 1. These findings align with previous studies (e.g., Bajda et al., 2004; Bektaş & Kara, 2004; Günay et al., 2007; Inglezakis et al., 2007; Mozgawa & Bajda, 2005; Mozgawa et al., 2009; Oter & Akcay, 2007), confirming that clinoptilolite exhibits excellent sorption capacity for Pb(II), removing over 98% of lead from solutions containing up to 1000 mg Pb/L. At higher initial concentrations, approximately 82% and 44% of Pb(II) were removed from solutions containing 2000 mg/L and 4000 mg/L, respectively (Table 1).

The greatest Pb uptake occurred in the experiment with an initial concentration of 4000 mg Pb/L, where 1714 mg Pb/L was removed from solution. The sorption capacity, calculated from the difference in Pb concentration before and after the experiment, reached approximately

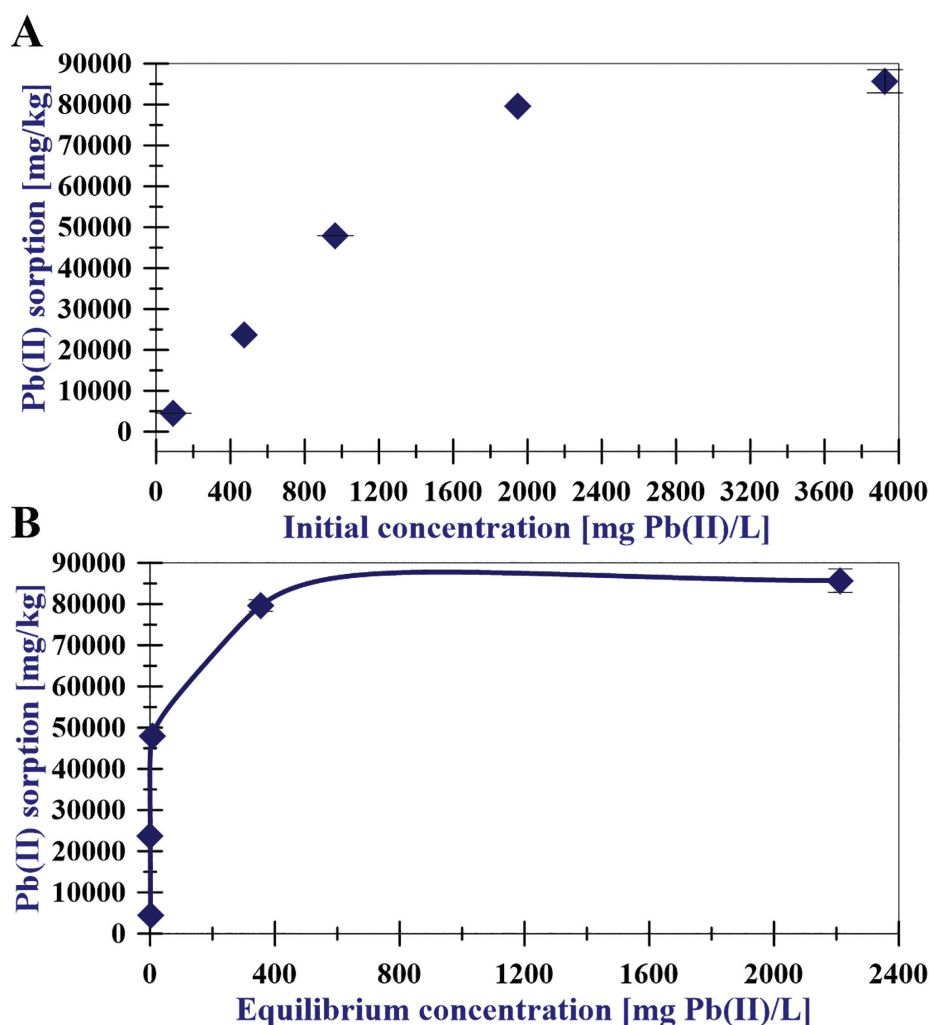


Figure 1. (A) Sorption of Pb(II) by clinoptilolite as a function of the initial Pb(II) concentration in solution. (B) Sorption isotherm of Pb(II) on clinoptilolite, illustrating the relationship between equilibrium Pb(II) concentration and the amount sorbed.

Table 1. Results of Pb(II) sorption by natural clinoptilolite

Initial assumed concentration [mg Pb/L]	Initial measured concentration [mg Pb/L]	Equilibrium concentration [mg Pb/L]	Difference between initial and equilibrium concentration	Amount of Pb [mg] sorbed by 0.8 g of zeolite	Amount of Pb [mg] per 1 kg of zeolite	Pb Removal [%]
100.0	92.0	1.6	90.4	3.6	4520.0	98.3
500.0	473.4	<0.5	472.9	18.9	23,645.0	99.9
1000.0	966.0	7.4	958.6	38.3	47,930.0	99.2
2000.0	1948.0	355.0	1593.0	63.7	79,650.0	81.8
4000.0	3926.0	2212.0	1714.0	68.6	85,700.0	43.7

Results were obtained using AAS.

AAS, atomic absorption spectroscopy.

85,700 mg Pb/kg of zeolite. The Pb-sorbed zeolite was subsequently washed repeatedly with redistilled water until the Pb concentration in the rinsate dropped below 0.1 mg/L and then air-dried. Chemical analysis of the solid revealed that the amount of non-desorbed lead retained by the zeolite was 74 g Pb/kg. Given this high uptake capacity, this material was selected for subsequent experiments.

3.2. Arsenate sequestration by reaction with Pb-modified zeolite

The reaction of Pb-modified zeolite (Fig. 3a) with a solution containing AsO_4^{3-} and Cl^- ions at initial pH values of 2 and 7 resulted in the immediate crystallization of lead chloro-arsenate (mimetite, $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$; Figures 2b and 3b), effectively sequestering arsenate from the solution. Mimetite was detected by XPRD after the experiment. A comparison of XPRD patterns before and after exposure to the arsenate—and chloride—containing solution confirmed that zeolite (containing admixtures of orthoclase, quartz, and illite) and mimetite were the only crystalline phases present (Fig. 2). Mimetite precipitated heterogeneously as needle-like crystals on the zeolite surface (Fig. 3c), partially covering most of the grains and forming incrustations (Figs. 3c, d). Additionally, some mimetite crystals crystallized near the primary phase but not directly on its surface, suggesting homogeneous precipitation. These crystals reached a size of up to 2.5 μm (Fig. 3e).

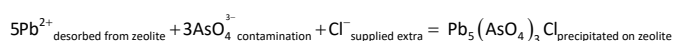
Arsenate removal varied significantly, reaching 67.7% at pH 2 but increasing to 99.88% at pH 7 within 24 hr. After 7 days, uptake at the more acidic pH improved to 74.84%, indicating a time-dependent process that may involved gradual mimetite formation, while at neutral pH, it remained unchanged (Table 2). The effect of pH can be attributed to both the stability of the mimetite ($\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$) phase and the predominant arsenate species present in solution. Mimetite exhibits higher stability at neutral pH, remaining a solid phase that effectively sequesters arsenate from the solution (Bajda, 2010; Magalhães & Silva, 2003). At low pH, Pb-modified zeolite may have partially dissolved, releasing Pb^{2+} into the solution, which could lead to re-dissolution or hindered precipitation of mimetite, resulting in lower arsenate retention.

Furthermore, arsenate speciation may have played a crucial role in the precipitation process. At pH 7, arsenate exists primarily as HAsO_4^{2-} , which readily interacts with Pb^{2+} , favouring mimetite formation. In contrast, at pH 2, arsenate is predominantly in the neutral H_3AsO_4 form, which has a lower affinity for Pb^{2+} , potentially limiting the precipitation reaction (Bajda, 2010; Smedley & Kinniburgh, 2002). These findings highlighted the importance of pH in controlling arsenate removal efficiency.

After 7 days of reaction in the presence of AsO_4^{3-} , the lead concentration ranged from <0.02 mg/L at pH 7 to 20 mg/L at pH 2. In contrast, in the control experiment, where Pb-modified zeolite was dissolved under identical conditions but in the absence of arsenate (only Cl^- was present), lead release was significantly higher, reaching 43 mg/L at pH 2. This is consistent with substantial zeolite dissolution under acidic conditions. The Pb concentration remained significantly lower at higher pH levels, at 0.61 mg/L.

The ionic strength and pH of the solution influence not only the efficiency of heavy metal sorption but also the stability of zeolite and the potential re-release of contaminants into the medium (e.g., Cama et al., 2005; Deliyanni et al., 2003; Payne & Abdel-Fattah, 2004, 2005; Wilkin & Barnes, 1998). At low pH, Pb concentrations greatly exceeded the drinking water standard of 0.01 mg/L, indicating significant mobilization of this toxic heavy metal into solution. In contrast, Pb levels remained below the detection limit of the AAS method, suggesting favourable conditions for practical arsenate sequestration under neutral conditions. Additionally, since the tested solutions contained only arsenate and/or chloride ions, the release of Pb may be less significant in more complex water compositions. The increased arsenate sequestration and minimal lead release at neutral pH conditions suggest that Pb-modified zeolite could be particularly effective in arsenic-contaminated waters with moderate pH levels.

Mimetite crystallized due to the reaction of Pb(II) desorbed from zeolite with arsenate and chloride ions present in aqueous solution:



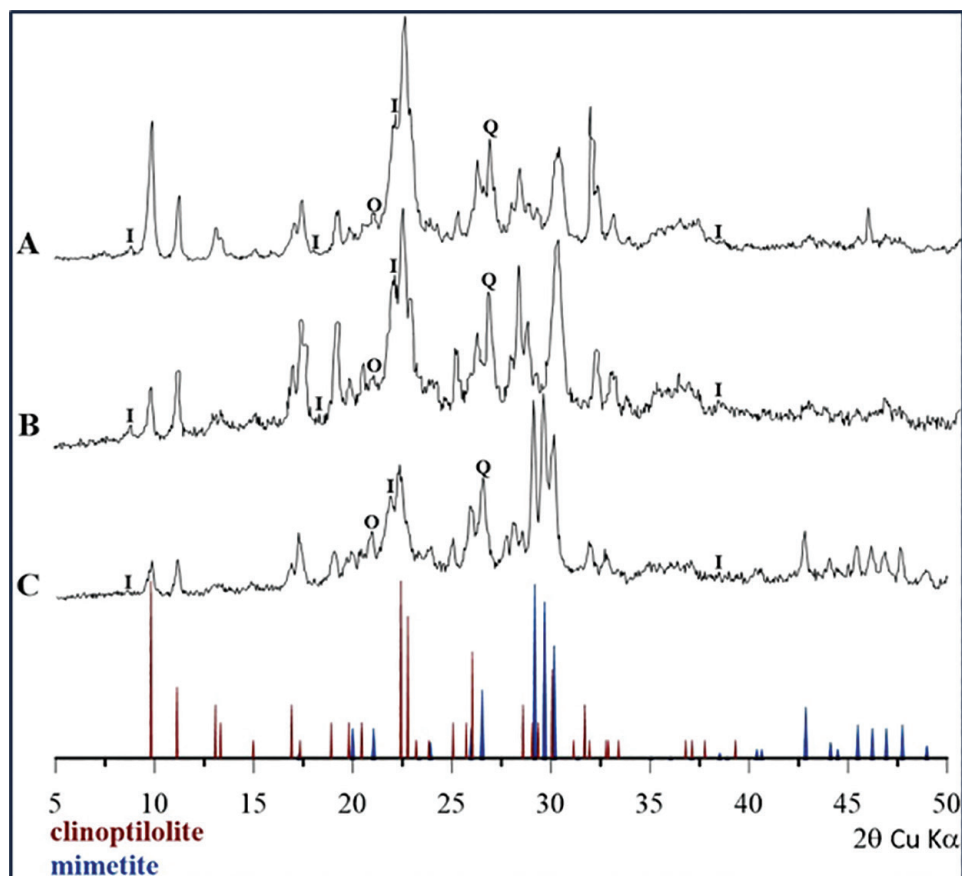


Figure 2. XPRD patterns of: (A) Natural zeolite (clinoptilolite) enriched in admixtures of orthoclase (O), illite (I), and quartz (Q), (B) Clinoptilolite after modification through sorption of Pb(II) and (C) Precipitate resulting from reaction of Pb-modified zeolite with AsO_4^{3-} aqueous solution at pH 7 (50 mg As/L). XPRD, X-ray powder diffraction.

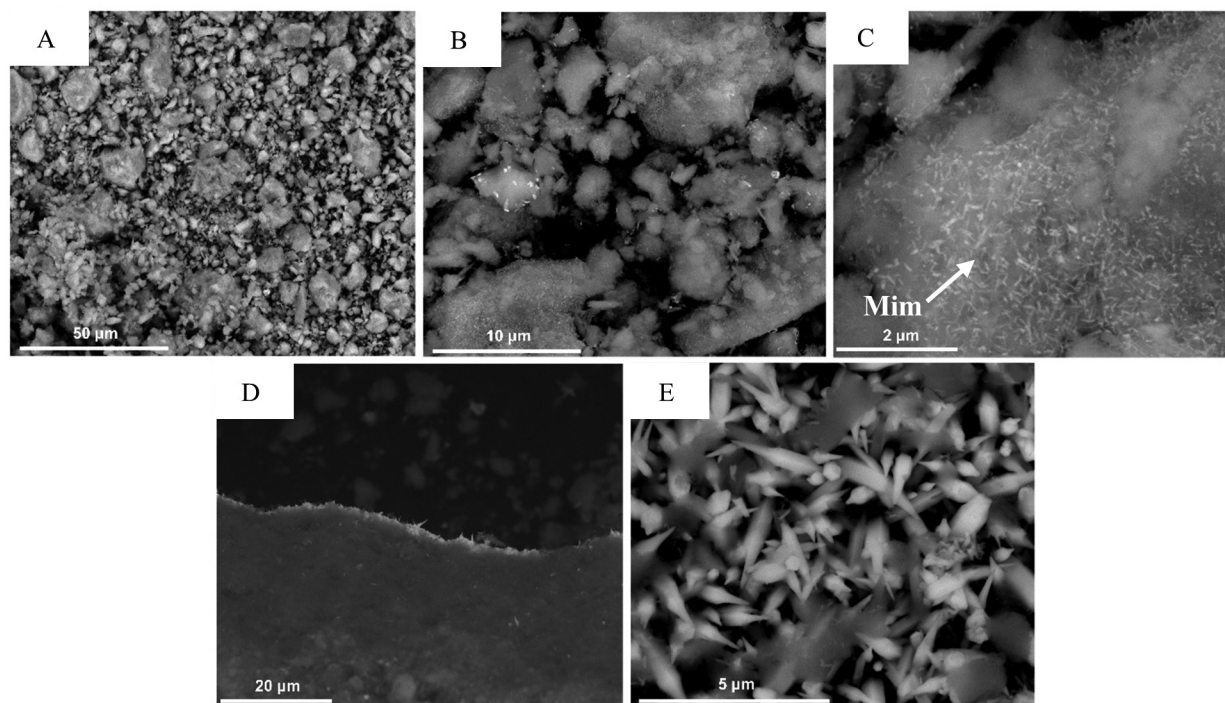


Figure 3. SEM images in BSE mode display the morphology of Pb-modified clinoptilolite and mimetite precipitates. (A) Pb-modified clinoptilolite, before reaction with an arsenate solution, exhibited a granular surface structure. (B) After reaction with an arsenate solution (50 mg As/L; pH 7) containing Cl^- ions (20 mg Cl^-/L), mimetite ($\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$) precipitated. (C) Lead chloro-arsenate formed as needle-like crystals distributed across the surface of the Pb—modified zeolite. (D) These needles developed as incrustations enveloping the grains of the primary Pb-clinoptilolite. (E) The mimetite needles reached lengths of approximately 2.5 μm , exhibiting characteristic hexagonal cross-sections. BSE, backscattered electron; SEM, scanning electron microscopy.

Table 2. Final concentrations of arsenic (As) and lead (Pb), along with arsenic removal efficiency, after a 7-day reaction between Pb-zeolite and As solution in the presence of chloride ions (20 mg/L)

Arsenic Removal Experiment				
Initial pH	Equilibrium pH	Initial [As] = 50 mg/L		
		Final [As] mg/L	Removal rate %	Final [Pb] mg/L
2.0	2.8	12.58	74.84	20.00
7.0	6.3	0.07	99.88	<0.02
Control experiment				
Initial pH	Equilibrium pH	Initial [As] = 0 mg/L		
		Final [Pb] mg/L		
2.0	2.7	42.47		
7.0	6.4	0.61		

The control experiment, also conducted in a chloride-containing system, shows Pb release from Pb-zeolite in the absence of As.

The solution likely became oversaturated immediately upon mixing, resulting in the precipitation of lead chloro-arsenate. The Pb-modified zeolite served as a nucleation substrate, providing active sites for the formation of the secondary phase. These sites facilitated local solution supersaturation with respect to mimetite ($\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$), promoting the heterogeneous precipitation (incrustations) of new phase crystals. When the local concentrations of lead, arsenate, and chloride ions in the bulk solution in the vicinity of zeolite reached a certain level, mimetite could precipitate within the solution volume, independent of the zeolite surface. Under these conditions, homogeneous nucleation of mimetite occurred, with crystals forming in the liquid phase and subsequently precipitating in the spaces between zeolite grains rather than as a layer on the substrate surface.

The Pb-modified zeolite served as the sole source of Pb(II) required for mimetite precipitation. While lead does not desorb from the zeolite in pure water, the presence of Na^+ , As(V) , and Cl^- in solution promoted the formation of mimetite. Lead desorption is likely facilitated by ion exchange with Na^+ ions, which replace Pb^{2+} in the zeolite structure. Additionally, the local depletion of Pb^{2+} at the mineral-water interface near the zeolite surface, driven by mimetite precipitation, may further promote lead release from the zeolite. The reaction predominantly occurs at the zeolite surface, suggesting that the rate of mimetite crystallization exceeds that of Pb^{2+} desorption. However, both euhedral crystals of mimetite and incrustations on the surface of zeolite were observed, indicating homogeneous and heterogeneous precipitation. Initially, desorbed Pb^{2+} reacted with AsO_4^{3-} and Cl^- available in the vicinity of the zeolite grains, resulting in heterogeneous precipitation and the formation of mimetite incrustations on the zeolite surface (Figs. 3b–d). This suggests that the desorption of lead was slower than the precipitation of mimetite. Once the local supply of AsO_4^{3-} and Cl^- was depleted, desorbed Pb^{2+} ions migrated into the bulk solution, leading to homogeneous precipitation of mimetite as needle-like crystals with hexagonal cross-sections, dispersed

between the clinoptilolite grains (Fig. 3e). In this case, supersaturation and subsequent precipitation occurred within the bulk solution. A similar phenomenon was reported for mimetite precipitation on goethite (Kleszczewska-Zębala et al., 2016). These observations imply that the advection of AsO_4^{3-} and Cl^- ions was slower than the desorption of Pb^{2+} . Arsenate and chloride ions were supplied by diffusion and advection from mixing the suspension. Slow diffusion enabled the distribution of lead ions necessary for mimetite crystallization on Pb-zeolite (Kleszczewska-Zębala et al., 2016; Manecki et al., 2006).

The presence of aqueous AsO_4^{3-} and Cl^- and precipitation of mimetite may have induced lead desorption in two ways. Firstly, the precipitation of mimetite acted as a trap for Pb ions in the solution, altering the equilibrium between lead-bound zeolite and the surrounding solution. This could increase the Pb desorption by Le Chatelier's principle. Furthermore, the interaction between arsenate ions and surface-sorbed lead may have weakened the bond between the lead and the surface, leading to its desorption and subsequent precipitation as mimetite.

4. Conclusions

The innovative application of lead-modified zeolite for arsenate removal through the induced precipitation of mimetite showed great potential for efficient and environmentally sustainable water treatment. The process of preparing zeolite via lead sorption was quick, straightforward, and effective. The induced formation of mimetite occurred rapidly and efficiently reduced the relatively high arsenate concentration in the aqueous solution, achieving a sequestration efficiency of up to 99%. The lead bound to the zeolite surface exhibited an optimal binding strength—sufficient to prevent lead desorption in clean water, yet weak enough to enable its reaction with arsenate and chloride ions in the solution. The experiments indicated that neutral pH provided the optimal conditions for mimetite formation. Imaging of the precipitate's morphology by scanning electron microscopy (SEM) revealed that the reaction primarily occurred directly on the zeolite surface, indicating that mimetite precipitation was faster than Pb desorption. To fully evaluate the potential of this method, additional studies will be conducted to examine the effects of other parameters, including ionic strength, competing anions, and reaction kinetics over extended periods, on arsenate sequestration from natural solutions and subsequent Pb stability.

5. Perspectives

The results presented here successfully proved the concept of a novel two-step approach to arsenate sequestration by mimetite precipitation on Pb-modified zeolite. This method, which combines adsorption-based material preparation with mineral transformation, offers a potentially robust and cost-effective solution for arsenic removal from water. Crystallisation of a thermodynamically stable mineral phase can reduce the

risk of arsenic remobilisation and improve long-term sequestration.

Future research should assess the system under more complex aqueous solution chemical conditions, evaluate the durability and reusability of the Pb zeolite material and investigate the safe disposal or reuse of the As-containing product. To support practical application, the method could be integrated into a modular treatment train comprising five units: (1) pre-filtration and pre-treatment (including oxidation and Cl^- addition), (2) arsenic removal using Pb-modified zeolite, (3) Pb-release control, (4) pH adjustment via liming to remove co-occurring metals, and (5) a quality control module. Such a system would allow for flexible deployment, independent regeneration of modules, and improved long-term sustainability, particularly in decentralized or passive treatment contexts.

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Declarations

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