Sorption of arsenate on ettringite formed in sulphate removal from mine drainage water

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Abstract

There is a current need for effective treatment methods for water pollutants such as sulphate and arsenic. Circular economy thinking is also increasing. Ideally, waste from one stream could be valuable in another. The aim of this research was to investigate arsenate sorption on ettringite formed in sulphate removal from underground gold mine drainage water. Batch sorption experiments were conducted at room temperature using a synthetic solution with an initial As(V) concentration of 1.7 ± 0.1 mg/L, which was chosen to model typical arsenate containing mine water. The effect of ettringite dosage was studied, and Langmuir and Freundlich sorption isotherms were fitted to the results. The maximum sorption capacity (1.8 mg/g) of the ettringite was determined from the Langmuir isotherm, which corresponded well with the maximum experimental sorption capacity. Furthermore, the effect of contact time was studied, and pseudo-first order and pseudo-second order kinetic models were fitted to the experimental data. The kinetics of the arsenate sorption on ettringite were best described by the pseudo-second order model. This paper offers one possible method of extracting value from mine water, as its results indicate that the precipitate produced during sulphate removal from mine water by precipitation as ettringite could be further used as a sorbent for arsenate removal from aqueous solutions.

Key words: Mine water, sulphate removal, ettringite, sorption, arsenic removal

Introduction

Sulphate emissions cause environmental problems. Mine water can contain up to tens of thousands of milligrams of sulphate per litre, and must be treated before discharge from a mine site. Precipitation as ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$) is an efficient method of sulphate removal from mine water. In this method, the pH of mine water is raised to approximately 12 using lime, and conventional aluminium chemical is added in order to precipitate sulphate as ettringite. For example, quicklime or hydrated lime and sodium aluminate or aluminum hydroxide can be used. The purified water can be treated with carbon dioxide (CO_2) precipitating calcite ($CaCO_3$) to lower the pH so as to be in accordance with mine discharge limits. With precipitation as ettringite, mine water sulphate concentration can be reduced to less than 200 mg/L (i.e., less than the drinking water guideline in Finland). In comparison, the conventionally used lime treatment (Tolonen et al. 2014, Tolonen et al. 2015) can reach sulphate levels of only 1500—2000 mg/L. When ettringite precipitation is used for waters with high sulphate concentration (>3000 mg/L), it may be economical to use traditional lime precipitation as a pre-treatment to remove some of the sulphate. After partial sulphate removal, a smaller dosage of the more expensive aluminium chemical is required for the ettringite precipitation step. Sulphate removal from mine water with precipitation as ettringite offers a means of reducing environmental pollution and simultaneously recovering a useful mineral that could be used, for example, as a construction material or as a sorbent in arsenic removal from water.

As arsenic is toxic and carcinogenic, arsenic contamination in natural waters is a significant problem. The World Health Organisation (WHO) has set a 0.01 mg/L guideline for arsenic in drinking water, which is the same value set as the permissible limit for drinking water in Finland. Arsenic occurs in the aqueous environment mainly at two oxidation states: arsenite As(III) and arsenate As(V). As(III) is 10 times more toxic than As(V). Eh and pH conditions control arsenic speciation. As(III) is dominant

at intermediate to low redox potentials, whereas As(V) is dominant at high redox potentials. Arsenic is a significant mine water contaminant that mainly occurs as As(V) in acid mine drainages (AMD) (Williams 2001, Bednar et al. 2004, Paikaray 2015). While the sorption of arsenate on ettringite has been studied by Myneni et al. (1997), to our knowledge, there are no studies of isotherm and kinetic models fit to data obtained from arsenate sorption experiments on ettringite.

In this research, arsenate sorption on ettringite that formed during sulphate removal from underground gold mine drainage water by adding hydrated lime and sodium aluminate was investigated. The sorption experiments were conducted using synthetic solution with 1.7 ± 0.1 mg/L As(V), which was chosen to model arsenic containing mine water. The effect of sorbent dosage was studied, and Langmuir and Freundlich isotherm models were fitted to the experimental data using OriginPro software. Futhermore, the effect of contact time was studied, and pseudo-first order and pseudo-second order kinetic models were fitted to the data from the experiments using OriginPro software.

Materials and methods

Ettringite

The sorbent (referred to as ettringite) that was used in the sorption experiments contained approximately 90 % ettringite and 10 % calcite, which was determined via quantitative X-ray diffraction data Rietveld analysis. The ettringite formed during sulphate removal from ferric sulphate treated mine drainage water from an underground gold mine (sampled after settling pond). The initial sulphate concentration of the mine drainage water was 1400 mg/L. The sulphate precipitation was done in batch-mode using programmable paddle stirrer equipment at room temperature (20 ± 2 ∘C). The sample volume was 800 mL for each 1 L glass beaker, with 1.5 g/L of hydrated lime (JT Baker 93+ %) and 0.5 g/L of sodium aluminate (Eka WT A 83, 40—50 % $NaAlO_2$) used as reagents. Each batch was mixed at 50 rpm for 5 hours and then left to settle overnight. The precipitates were filtered with Schleicher & Schuell 589 blue ribbon quantitative low ash filter paper by vacuum filtration. They were then air-dried, weighed, crushed, sieved to a 63—125 μm particle size fraction, and stored in a desiccator prior to the sorption experiments.

The sorption of arsenate on ettringite

The effect of the sorbent dosage on arsenate removal from synthetic solution was studied via 24 h batch sorption tests using a reciprocal shaker at room temperature (20 ± 2 ∘C). An arsenate model solution was prepared by dissolving arsenic (V)oxide (Acros Organics 99.9+ %) into ultrapure water. Then, 0, 0.2, 0.5, 1, 2, 3, 4, 5, 7 or 10 g/L of the synthesized ettringite was dosed to 0.025 L of 1.7 mg/L arsenate model solution and agitated at 250 rpm for 24 h in a reciprocal shaker (POL-EKO LS 700). After shaking, the samples were centrifuged at 4000 rpm for 5 min with Thermo Scientific SL 8 Centrifuge, after which the supernatant pH was measured. The supernatant was saved for arsenic analysis. The arsenic concentration was analysed using inductively coupled plasma optical emission spectrometry ICP-OES according to the standard SFS-EN ISO 11885 in an accredited laboratory (Ahma Ympäristö, Finland). Furthermore, the effect of contact time was also studied. One litre of the 1.8 mg/L arsenate model solution was stirred at 250 rpm in a 2 L glass beaker with a magnetic stirrer, and 1 g/L of ettringite was dosed into the solution. Samples were taken at 0, 1, 3, 5, 7, 10, 30 minutes, as well as 1, 2, and 5 hours after ettringite addition. The samples were centrifuged for 1 min at 4000 rpm, and the supernatant was saved for arsenic analysis.

Results and discussion

The effect of ettringite dosage

Figure 1 shows the As(V) removal percentages as a function of ettringite dosage. The As(V)removal percentage increases as the ettringite dosage increases from 0 to 4 g/L and then stabilizes thereafter. With a 4 g/L ettringite dosage, an arsenic concentration below the drinking water limit was obtained. However, the increase of sorption efficiency after 1 g/L dosage was quite moderate. The best arsenate removal from the techno-economical point of view (90 %) was obtained with a 1 g/L ettringite dosage.
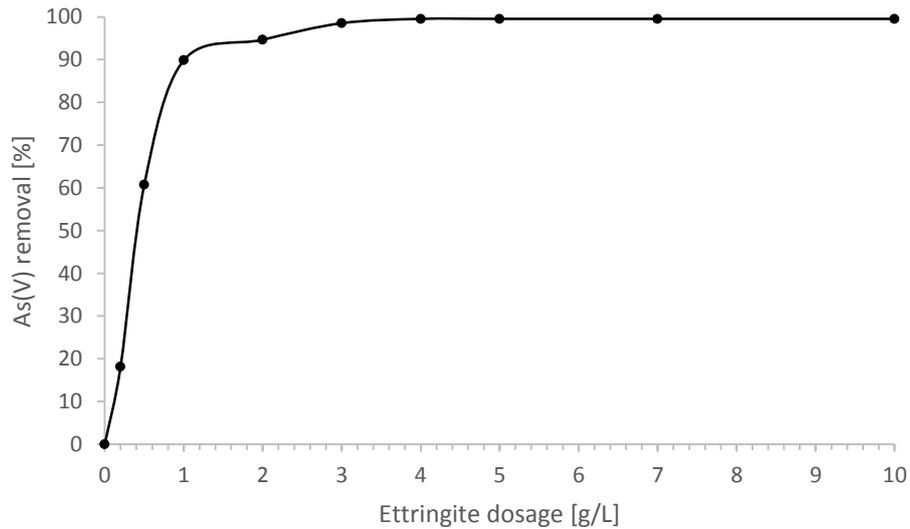
Figure 1 *The effect of sorbent dosage on the sorption of arsenate on ettringite. Initial As(V) concentration = 1.7 mg/L, ettringite dosage = 0—10 g/L, temperature = 20 ± 2 ∘C, agitation = 250 rpm, contact time = 24h, and solution volume = 25 mL. Values are presented as the average of duplicate experiments.*

Isotherms

Figure 2 shows Langmuir and Freundlich isotherm models fitted to the data gained from the experiments concerning the effect of ettringite dosage on arsenate removal. The Langmuir (1918) and Freundlich (1906) isotherms, which are the most commonly used isotherm models, are represented by the following equations 1 and 2, respectively. The Langmuir isotherm model assumes monolayer sorption that occurs on a homogenous surface with no interactions between sorbates. The Freundlich isotherm model is empirical and assumes that sorption occurs on a heterogenous surface.

$$q_e = \frac{Q_{max} b c_e}{1 + b c_e} \tag{1}$$

$$q_e = K c_e^{\frac{1}{n}} \tag{2}$$

where q_e (mg/g) is the amount of arsenate sorbed on ettringite at equilibrium, Q_{max} (mg/g) Langmuir isotherm constant relating to maximum sorption capacity, b (L/mg) Langmuir isotherm constant relating to the energy of sorption, c_e (mg/L) the equilibrium solution concentration, K (L/g) Freundlich isotherm constant related to sorption capacity, and 1/n Freundlich isotherm constant relating to intensity of sorption.

The fit of each isotherm model was compared according to the adjusted correlation coefficient R^2_{adj} values. The Langmuir and Freundlich isotherms fitted equally well to the experimental data. The isotherm parameters are presented in Table 1. The Freundlich parameter 1/n was < 1, indicating favourable sorption. The maximum sorption capacity obtained from the Langmuir isotherm was 1.8 mg/g, which was in the same range as the maximum experimental adsorption capacity. The low initial arsenate concentration used in the experiments could be the cause of the relatively low sorption capacity. A similar observation was made by Luukkonen et al. (2016) for the sorption of arsenite on geopolymers. The experimental equilibrium sorption capacity was calculated according to equation 3 as follows:

$$q_e = \frac{(c_0 - c_e) \cdot V}{m_{ads}} \tag{3}$$

where c_0 (mg/L) is the initial solution concentration, c_e (mg/L) the equilibrium solution concentration, V (L) the volume of the solution, and m_{ads} (g) the amount of the sorbent.
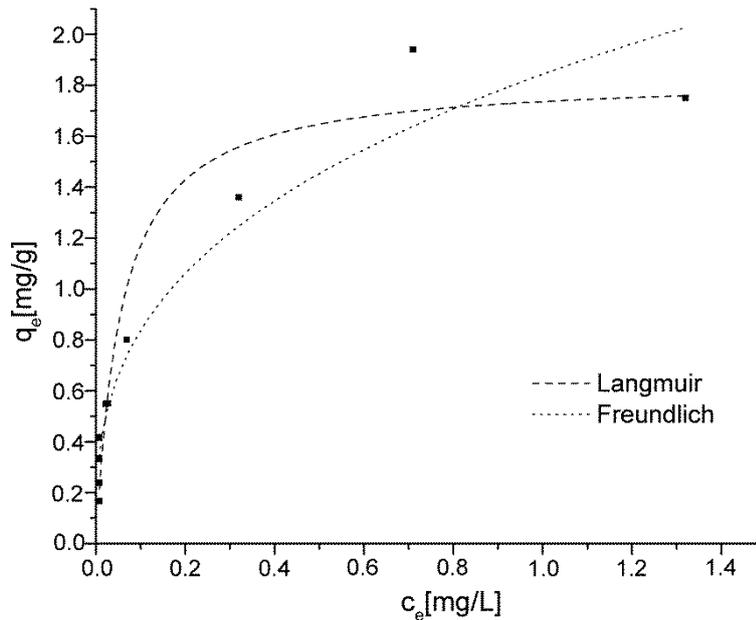

Figure 2 Isotherm for the sorption of arsenate on ettringite, and the fit of the Langmuir and Freundlich models. Initial As(V) concentration = 1.7 mg/L, ettringite dosage = 0—10 g/L, and temperature = 20 ± 2 ∘C.

Table 1 *Isotherm parameters.*

Parameter	Langmuir	Parameter	Freundlich
Q_{max}	1.835	K	1.844
Standard error of Q_{max}	0.109	Standard error of K	0.101
b	17.616	n	2.914
Standard error of b	3.619	Standard error of n	0.249
R^2	0.943	R^2	0.937
R^2_{adj}	0.938	R^2_{adj}	0.932
reduced chi-square, X^2_{red}	0.022	reduced chi-square, X^2_{red}	0.024
residual sum of squares, RSS	0.259	residual sum of squares, RSS	0.284
root mean square error, RMSE	0.147	root mean square error, RMSE	0.154

The effect of contact time and kinetic modelling

Figure 3 shows arsenate removal as a function of time. In the beginning of this process, the uptake of arsenate on ettringite was rapid, which was due to many available sorption sites on the surface of the ettringite for arsenate sorption. However, the sorption later proceeded at slower rate and reached equilibrium within 10 minutes contact time. Thus, the saturation of the sorption sites on the surface of ettringite led to the slower rate of arsenate sorption as time passed.
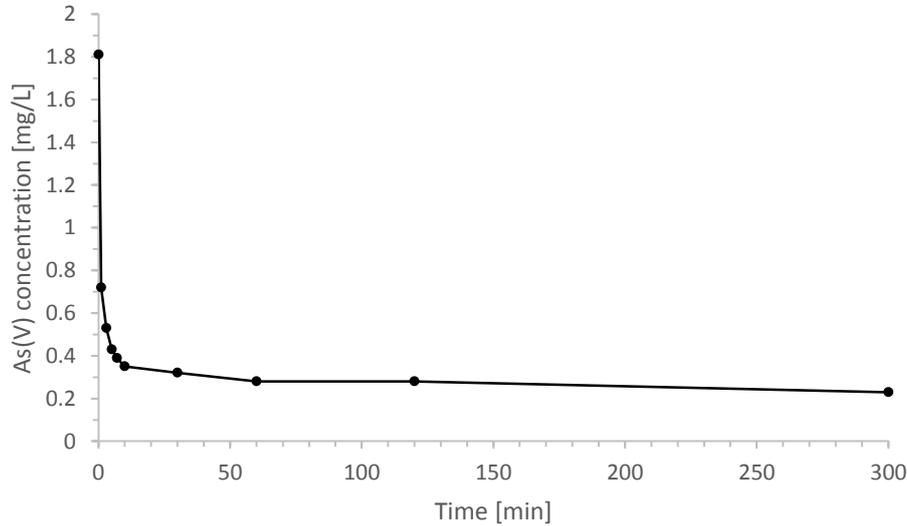

Figure 3 The effect of contact time on the sorption of arsenate from a model solution on ettringite. Initial arsenate concentration = 1.8 mg/L, ettringite dosage = 1 g/L, temperature = 20 ± 2 °C, initial solution volume = 1 L, stirring 250 rpm, and samples taken between 0-5 h.

Figure 4 shows the pseudo-first order and pseudo-second order kinetic models that were fitted to the experimental data. The Lagergren pseudo-first order model (1898) and the pseudo-second order model (Ho and McKay 1999) are represented by equations 4 and 5, respectively.

$$q_t = q_e \left(1 - e^{-k_1 t} \right) \tag{4}$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{5}$$

where k_1 (1/min) is the pseudo-first order rate constant, k_2 ((g/(mg*min)) the pseudo-second order rate constant, q_e (mg/g) the amount of arsenate sorbed on ettringite at equilibrium and q_t (mg/g) the amount of arsenate sorbed on ettringite at time t (min).

The parameters of the kinetic models are presented in Table 2. The fit of the models was evaluated by comparing the adjusted correlation coefficient R^2_{adj} values. Following this, the pseudo-second order model was found to best fit the experimental data. The adsorption capacity obtained from the pseudo-second order model was 1.5 mg/g, which was in agreement with the experimental equilibrium adsorption capacity value.
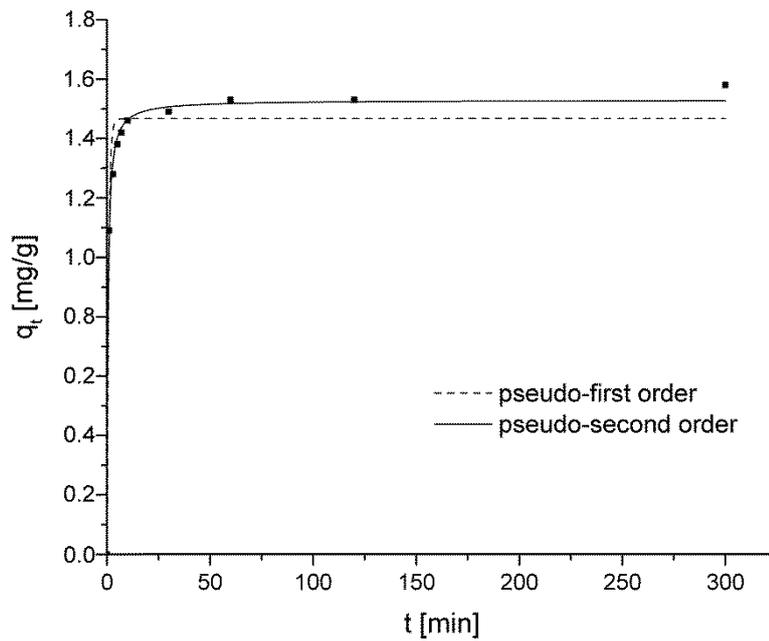
Figure 4 *Pseudo-first order and pseudo-second order kinetic models fitting for the sorption of arsenate on ettringite. Initial As(V) concentration 1.8 mg/L and ettringite dosage 1 g/L.*

Table 2 *Parameters from the kinetic models.*

Parameter	Pseudo-first order	Parameter	Pseudo-second order
q_e	1.467	q_e	1.530
Standard error of q_e	0.030	Standard error of q_e	0.014
k_1	1.257	k_2	1.437
Standard error of k_1	0.206	Standard error of k_2	0.146
R^2	0.972	R^2	0.996
R^2_{adj}	0.969	R^2_{adj}	0.996
reduced chi-square, X^2_{red}	0.007	reduced chi-square, X^2_{red}	0.001
residual sum of squares, RSS	0.056	residual sum of squares, RSS	0.008
root mean square error, RMSE	0.083	root mean square error, RMSE	0.031

Conclusions

The results of this study indicate that ettringite formed during sulphate removal from mine water could be utilized as an arsenate sorbent. A ninety percent arsenate reduction from the initial 1.7 mg/L arsenate concentration was obtained with a 1 g/L ettringite dosage. The maximum sorption capacity of ettringite for As(V) obtained from the Langmuir isotherm was 1.8 mg/g. This relatively low sorption capacity could be due to a low initial arsenate concentration, which was chosen to model the arsenic-containing mine waters. The adsorption capacity of ettringite could possibly be increased with heat

treatment, but this would also increase the cost of the treatment. The sorption of arsenate on ettringite was fast, reaching equilibrium within 10 minutes. The Langmuir and Freundlich isotherm models fitted the sorption data equally well with an R^2_{adj} value of 0.94. The pseudo-second order model (R^2_{adj} > 0.99) best fitted the kinetic data of the arsenate sorption on ettringite.

Acknowledgements

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