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Removal of sulphate and arsenic from wastewater using calcium sulfoaluminate (ye'elimite)

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Chemical precipitation is one of the most widely known methods for treatment of industrial wastewaters with high sulphate content, where sulphate can be precipitated as practically insoluble ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$). This treatment method is also widely recognised for solidifying hazardous components and toxic elements e.g. arsenic in wastewater. In the ettringite precipitation process, lime and aluminium salts are typically used as starting materials, in stoichiometric amounts to form ettringite from the sulphate-containing water, leading to a pH rise to ~11.5 and ettringite precipitation. In the current study, for the first time, ye'elimite mineral ($Ca_4Al_6O_{12}SO_4$), also known as calcium sulfoaluminate (CSA) in cements, is used in order to investigate its suitability to form ettringite precipitate from sulphate and arsenic containing synthetic wastewater and industrial wastewater solutions. The dissolution of ye'elimite prior to dosing, optimal precipitation pH, and arsenic co-precipitation were studied. The effluent and precipitates were characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM-EDS) and inductively coupled plasma atomic emission spectroscopy (ICP-OES). The results showed that high percentage of sulphate removal (98% in the synthetic wastewater and 87% in the industrial wastewater) can be achieved using ye'elimite as the aluminium source in ettringite precipitation. Additionally, up to 95% arsenic removal was achieved in arsenic co-precipitation experiments from the synthetic wastewater. The current developed technology can be used as a novel ecological and cost-effective approach for removal of sulphate and toxic elements from wastewater.

KEYWORDS

ye'elimite, calcium sulfoaluminate, ettringite precipitation, sulphate removal, arsenic removal, industrial wastewater treatment

1 Introduction

Sulphate is a common major anion in industrial wastewaters formed in many industries, such as mining, metal, and pulp manufacturing (Jin et al., 2020). Sulphate anion (SO_4^{2-}) is not considered to be toxic; however, high sulphate content in discharge water can result in an increase in the salinity of receiving water, e.g., lake (Nariyan et al., 2018). The high concentration of sulphate in discharge water can also influence the permanent stratification of the receiving lake, hence disturbing nutrient and oxygen cycles (Boehrer and Schultze, 2008). Therefore, the industrial wastewater with high sulphate content are required to be treated prior to being discharged into the environment. Sulphate content limits for discharge water typically range between 250 and 1,000 mgL^{-1} SO_4^{2-} (Runtti et al., 2018). Residual sulphate concentration below these limits can be achieved using ettringite precipitation, due to the low solubility of ettringite. During the ettringite precipitation process, calcium hydroxide (also known as hydrated lime) and aluminium reagents, such as sodium aluminate are added to the sulphate containing water, leading to a pH rise to 10.5–13, and, hence precipitation of ettringite (Reinsel, 1999; Tolonen et al., 2016; Segundo et al., 2019). Additionally, ettringite is widely recognised to stabilise hazardous components and toxic elements, including heavy metals and borate ion (Arliguie and Grandet, 1990; Olmo et al., 2001; Weeks et al., 2008; Coumes et al., 2009; Coumes et al., 2017).

The crystalline structure of ettringite $(Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O)$ consists of $(Ca_6[Al(OH)_6]_2\cdot 24H_2O)^{6+}$ layers, where channels between these layers are occupied by SO_4^{2-} anions and water (H_2O) molecules (Myneni et al., 1998). Ettringite can bind oxyanions by mechanisms of interaction with the surface functional groups by ligand exchange or by substitution of sulphate anions in ettringite channels (Zhang and Reardon, 2003). The oxyanion binding properties of ettringite can be utilized for removal of arsenic and other impurities from water. Arsenic exists typically as oxyanion arsenate (AsO_4^{3-}) in alkaline conditions (Myneni et al., 1997; Zhang and Reardon, 2003). Arsenate anions are repelled by the negatively charged ettringite anions, while they are attracted to the positively charged $(Ca_6[Al(OH)_6]_2\cdot 24H_2O)^{6+}$ layers. Therefore, the surface charge and structure of ettringite indicate that substitution can be the main driving mechanism (Zhang and Reardon, 2003).

The typically used aluminium reagents, such as sodium aluminate are costly (Sapsford and Tufvesson, 2017; Tian et al., 2019). The choice of aluminium reagent has high impact on operational cost of the ettringite precipitation method. Alternatively, industrial by-products can be utilised as aluminium reagents during ettringite precipitation process, offering ecological benefits and lower costs (Álvarez-Ayuso and Nugteren, 2005). A cost effective sulphate removal process using an aluminium-based proprietary reagent has also been suggested in the literature (Reinsel, 1999). The selection of aluminium reagent influences the efficiency of sulphate removal, as well as sludge density and sludge settling velocity (Sapsford and Tufvesson, 2017).

Ettringite can also be produced using ye'elimite ($Ca_4Al_6O_{12}SO_4$), the representative hydraulic phase in calcium sulfoaluminate (CSA) cements (Haha et al., 2019). CSA-based clinker can be produced using industrial by-products and are intensively promoted as eco-friendly alternatives to Portland cement (PC), due to their potential to reduce carbon dioxide (CO_2) emissions and energy consumption up to 35% and 15%, respectively, compared to that of PC (Hanein et al., 2018; Haha et al., 2019). CSA cements are currently being developed for waste management solutions and applications. Additionally, the hydrated CSA cement matrix encapsulates toxic elements and heavy metals, which can be chemically bound and immobilized in ettringite and monosulfate phases (Albino et al., 1996; Berardi et al., 1998; Ambroise and Pera, 2004; Peysson et al., 2005; Luz et al., 2006; Zhou et al., 2006; Luz et al., 2007; Qian et al., 2008; Berger et al., 2009; Luz et al., 2009; Winnefeld and Lothenbach, 2010; Berger et al., 2011; Sun et al., 2011; Wu et al., 2011; Champenois et al., 2012; Mesbah et al., 2012; Champenois et al., 2015; Beltagui et al., 2017; Coumes et al., 2017).

Upon hydration, ye'elimite forms the main hydrates in CSA-based cement systems, including highly crystalline ettringite and partially disordered monosulfate, as well as amorphous aluminium hydroxide (Glasser and Zhang, 2001; Hargis et al., 2014). Hence, ettringite is formed in the presence of calcium, sulphate, and hydroxide in the aqueous solution (Fridrichová et al., 2016):

$$Ca_4Al_6O_{12}SO_4(s) + 8CaSO_4(aq) + 6Ca(OH)_2(aq) + 90H_2O(l) \rightarrow 3Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O(s)$$

In the present work, the suitability of ye'elimite, together with calcium hydroxide, to form ettringite precipitate from sulphate and arsenic containing synthetic wastewater and industrial wastewater solutions is investigated. Calcium hydroxide can be used unaccompanied to remove sulphate from water; however, in order to reduce SO_4^{2-} content within the acceptable limits of discharge water, the precipitation of insoluble ettringite is required. Sulphate removal efficiency and precipitate purity as well as, arsenic co-precipitation during ettringite precipitation were scrutinised.

2 Materials and methods

2.1 Materials

Sodium sulphate (VWR, 99.9%) and arsenic pentoxide (VWR, 99.9%) were used for preparation of synthetic wastewater solutions. Hydrochloric acid (VWR, 37%) and

TABLE 1 The chemical composition of industrial wastewater used in this study.

SO_4 (g/l)	Na (g/L)	Ca (g/L)	Mg (g/L)	Mn (mg/L)	Zn (mg/L)	Fe (mg/L)
16	1.9	0.53	2.5	260	309	<0.2

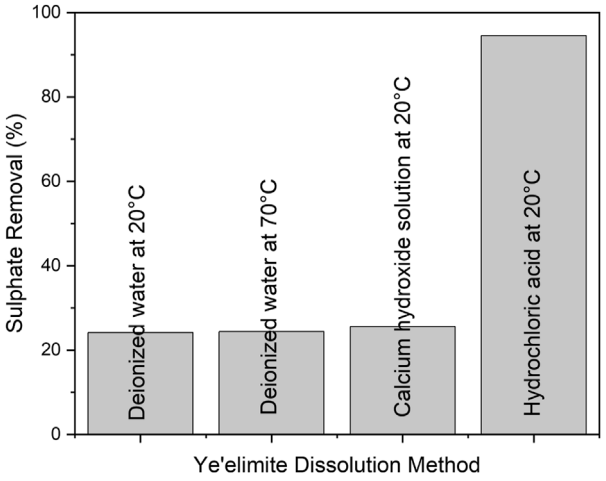

FIGURE 1
Percentage of sulphate removal from the synthetic wastewater using different ye'elimite dissolution methods.

calcium hydroxide (VWR, 98%) were used in the ettringite precipitation experiments. Calcium hydroxide was used at 10 wt% aqueous solution (2.045 g calcium hydroxide in 18 ml deionized water) in this study. 1 or 10 M sodium hydroxide solutions (Merck), were used in order to adjust pH of solutions. Aluminium oxide (Alfa Aesar, 99.7%), calcium sulphate (Alfa Aesar 99%), and calcium oxide (Alfa Aesar, 99%) were used to synthesize ye'elimite. The chemical composition of industrial wastewater used in this study is tabulated in Table 1.

2.2 Sample preparation

Three synthetic wastewater solutions were prepared by addition of 2.62 g sodium sulphate and a varying amount of arsenic pentoxide (0, 0.23, and 0.35 g) to 1 L deionized water, which corresponds to sulphate concentration of 2,000 ppm (including sulphate from ye'elimite) and arsenic concentrations of 0, 58, and 100 ppm (mg/L). The synthetic wastewater solution containing sodium sulphate in absence of arsenic pentoxide is referred to as "model solution" in this study.

Ye'elimite (250 g) was synthesized from stoichiometric amounts of aluminium oxide (50.1 wt%), calcium sulphate (22.3 wt%), and calcium oxide (27.6 wt%) at 1,300°C. The raw materials were dried at 800°C prior to firing and mixed by hand in a porcelain mortar for 20 min and added to an alumina crucible. The crucible was placed in a preheated (600°C) muffle furnace (Nabertherm Chamber furnace) and heated to 1300°C with the heating rate of 10°C/min, held for 4 h, and then slowly cooled down to room temperature during 4 h with the average cooling rate of 300°C/h. Ye'elimite was ground using a mortar and sieved using an air jet sieve (Alpine e200LS, Hosokawa Micron, Japan) with particle size of 125 μm. The purity of synthesized ye'elimite was 91.6% (Cuesta et al., 2013), containing minor phases of 5.8% krotite ($CaAl_2O_4$) (Hörkner and Müller-Buschbaum, 1976), and 2.6% anhydrite ($CaSO_4$) (Morikawa et al., 1975), as measured by Rietveld refinement (see Figure A1).

To achieve maximum sulphate removal efficiency, several dissolution methods for ye'elimite were tested. These include dissolving 1.2 g ye'elimite in 1) 11 ml deionized water at 20°C, 2) 11 ml deionized water at 70°C, 3) calcium hydroxide aqueous solution (2.0 g calcium hydroxide in 18 ml deionized water) at 20°C, and 4) 3 ml hydrochloric acid at 20°C, comprising four different dissolution methods. Ye'elimite was dissolved for 2 h using magnetic stirrer (1400 rpm) in each solutions and then was used as reagent in the ettringite precipitation experiments. Each of these ye'elimite containing solutions were then added separately to 800 of mL model solution simultaneously into four zones (dropwise during 5 min with 400 rpm) using a programmable paddle stirrer equipment (Kemira, Flocculator 2000).

For ettringite precipitation, the calcium hydroxide mixtures were added in stoichiometric ratio into the synthetic wastewater and industrial wastewater solutions (Ca: Al: SO_4 = 6: 2: 3). After addition of calcium hydroxide and ye'elimite, the pH was adjusted using the sodium hydroxide solutions. The samples were mixed at 50 rpm for 5 h, followed by overnight settling. After settling, the sludge volume was estimated and the precipitates were filtered using 7–12 μm filter paper *via* vacuum filtration. The filtered sludge was air-dried, crushed, sieved (63 μm), and stored in a desiccator. All the precipitation experiments were done duplicate.

2.3 Analytical techniques

All effluent samples were vacuum filtered through 0.45 μm cellulose nitrate membrane filters (Sartorius) prior to analysis.

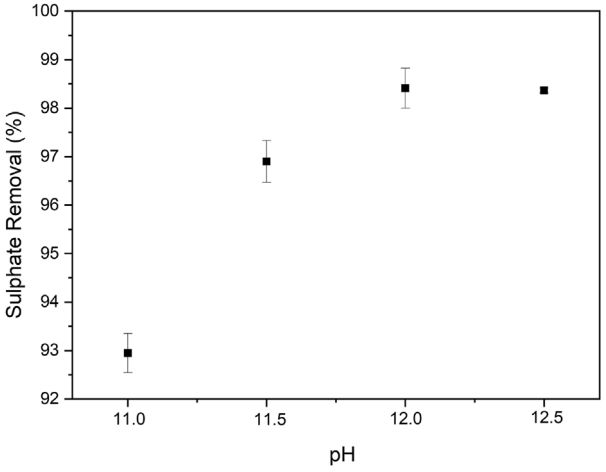

FIGURE 2
Percentage of sulphate removal from the model solution using different precipitation pH. Error bars represent standard deviation (n = 2).

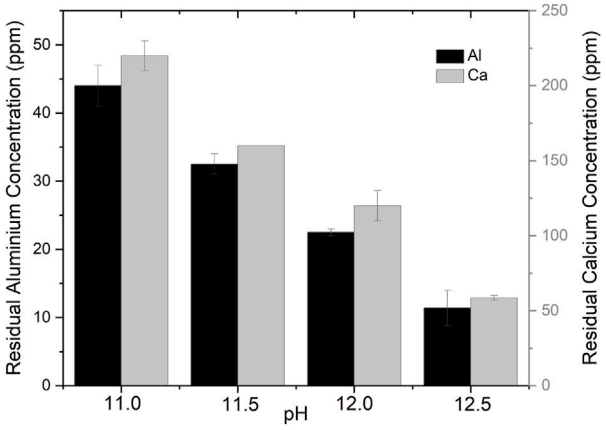

FIGURE 3
Residual aluminium and calcium concentrations with different precipitation pH. Error bars represent standard deviation (n = 2).

Aluminium, calcium, and arsenic elements were detected with an inductively coupled plasma atomic emission spectroscopy (ICP-OES). Sulphate was measured with an IC (METROHM 761 Compact IC, Herisau) following standard SFS-EN ISO 10304–1. Magnesium was measured using an atomic absorption spectrophotometer (AAS) (Varian AA240FS) based on standard SFS 3018. Both IC and AAS measurements were done triplicate. pH and conductivity of the effluent samples were measured using a HACH HQ40d portable meter and the turbidity was measured using an Oakton Portable Turbidimeter TN-100.

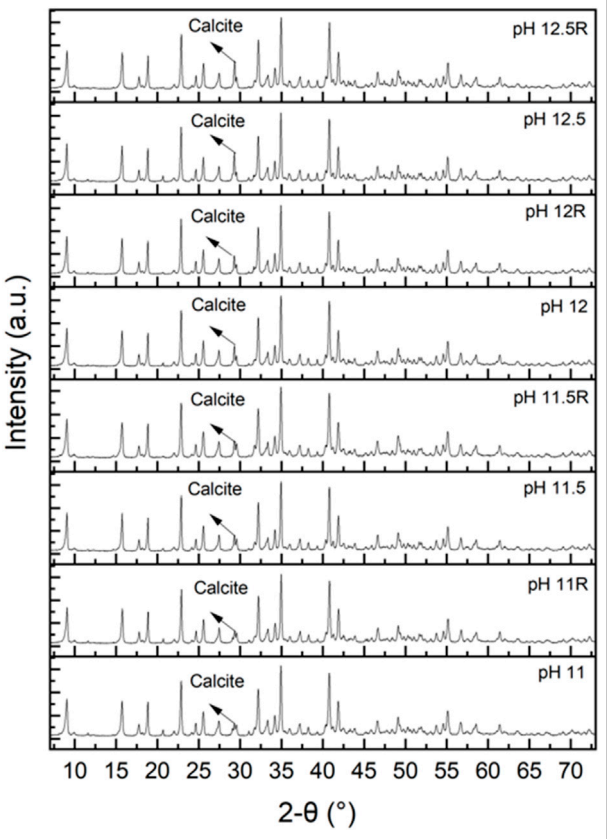

FIGURE 4
X-ray diffraction (XRD) patterns of precipitates from the ettringite precipitation experiments at pH range 11–12.5. R denotes repeated test. The unmarked peaks in the diffractograms are related to ettringite.

The synthesized ye'elimite was analysed using a SmartLab 9 kW diffractometer (Rigaku) equipped with D/teX Ultra 250 detector. X-ray diffraction (XRD) pattern was recorded with Co (Kα1 = 1.78892, Kα2 = 1.79278) at 40 kV and 135 mA in a range of 2-theta 5–130° with step size of 0.02° and scanning speed 4.063°/min. The phase quantities from XRD patterns were analysed with Rietveld method using PDXL 2 software (Rigaku, Japan) with PDF-4 + 2020 RDB database.

The dried precipitate samples were analysed with the PANalytical X'Pert PRO X-ray Diffractometer. The difractograms were collected using Cu Kα (1.5406 Å) source at 40 mA and 45 kV in the 2 Theta range of 5–70° and with a scan speed of 0.0235°/s. The XRD analysis was conducted using the HighScore program and Rietveld method.

Field emission scanning electron microscopy (FESEM-EDS) analysis of precipitates was conducted using a Zeiss Ultra plus operated at 15 kV with energy dispersive X-ray spectroscopy (EDS) detector and Aztec software (Oxford Instruments). Arsenic content in the precipitates from arsenic

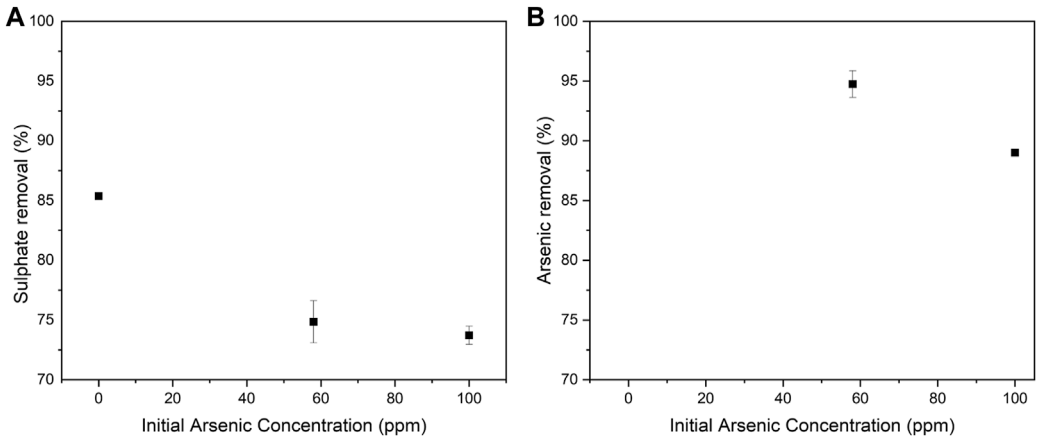

FIGURE 5
Sulphate **(A)** and arsenic **(B)** removal as a function of the initial arsenic concentration in the ettringite precipitation experiments using the synthetic wastewater solutions. Error bars represent standard deviation (n = 2).

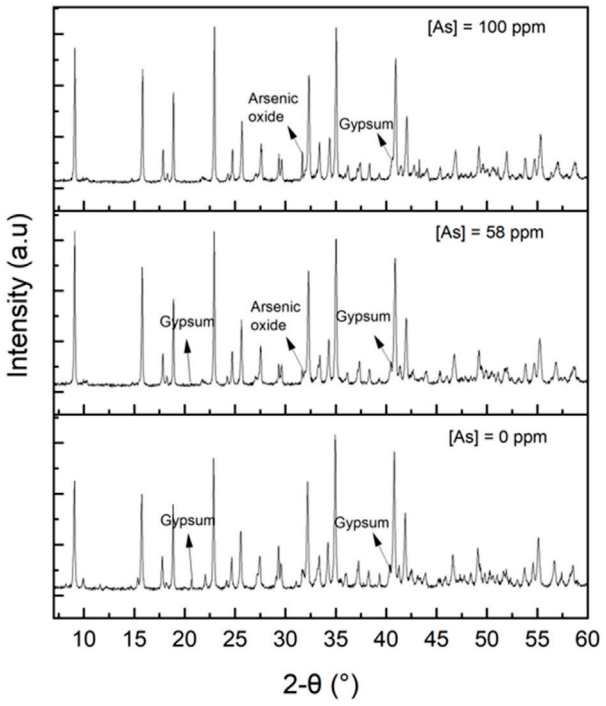

FIGURE 6
X-ray diffraction (XRD) patterns of the precipitates synthesized in the absence of arsenic, in the presence of 58 ppm arsenic, and 100 ppm arsenic.

coprecipitation experiments was measured using the ICP-OES. The analysis was conducted according to U.S. EPA Method 3051A, where the microwave-assisted wet digestion was performed using a 3:1 ratio of HNO_3 and HCl acid.

3 Results and discussion

3.1 Effectiveness of ye'elimite dissolution method

In order to examine the effectiveness of sulphate removal, different ye'elimite dissolution methods were tested. Figure 1 below shows the percentage of sulphate removal from the model solution (sodium sulphate containing synthetic wastewater in absence of arsenic pentoxide); i.e., when ye'elimite was dissolved in four different solutions: deionized water at 20 and 70°C, solution of 10 wt% calcium hydroxide in deionized water at 20°C, and hydrochloric acid at 20°C. As shown in Figure 1, the dissolution of ye'elimite in hydrochloric acid resulted in significantly higher sulphate removal (95%), indicating that almost all ye'elimite was dissolved and reacted in order to form ettringite, yielding the highest amount of ettringite (84%). Thus, the hydrochloric acid dissolution method of ye'elimite (described in Section 2.2) was selected for further investigations in this study.

3.2 pH optimisation of ettringite precipitation

pH is an important parameter in ettringite precipitation since ettringite is only stable in the pH range of 10.5–13 (Tolonen et al., 2016; Segundo et al., 2019). Four different pH values were tested for the ettringite precipitation experiment, including 11.0, 11.5, 12.0, and 12.5 (Figure 2). The current results show that the highest percentage of sulphate removal from the model solution was achieved at

TABLE 2 Al/S ratio in the precipitates from arsenic co-precipitation experiments.

Sample	Analysis number	As [wt%]	Al:S ratio	Analysis number	As [wt%]	Al:S ratio
0 ppm As	1	0	0.71	11	0	0.62
	2	0	0.51	12	0	0.57
	3	0	0.53	13	0	0.63
	4	0	0.78	14	0	0.51
	5	0	0.85	15	0	0.69
	6	0	0.63	16	0	0.69
	7	0	0.69	17	0	0.84
	8	0	2.85	18	0	0.68
	9	0	0.79	—	—	—
	10	0	0.59	—	—	—
58 ppm As	39	0.79	0.72	49	3.01	0.73
	40	2.37	0.90	50	2.76	0.71
	41	0.51	0.49	51	0.61	0.29
	42	0.7	0.69	52	2.84	0.74
	43	2.56	0.78	53	2.81	0.71
	44	2.45	0.73	54	2.67	0.71
	45	2.57	0.73	55	2.22	0.67
	46	2.59	0.74	56	2.18	0.63
	47	2.71	0.72	—	—	—
	48	1.35	0.54	—	—	—
100 ppm As	98	3.81	1.64	108	2.12	0.62
	99	0.49	0.91	109	0.46	0.48
	100	1.71	0.83	110	3.36	0.74
	101	4.26	0.78	111	0.62	0.88
	102	2.9	0.65	112	2.26	0.81
	103	0.39	1.10	113	2.75	0.79
	104	1.14	0.90	114	1.45	0.73
	105	0.32	1.02	115	0.63	0.73
	106	0.27	0.85	116	0.73	0.92
	107	0.54	0.33	117	0.54	0.86

pH 12–12.5. Similarly pH range of 11–12.5 was suggested for ettringite precipitation in the literature (Chrysochoou and Dermatas, 2006; Almasri et al., 2015). As shown in Figure 3, pH 11.0 was too low to effectively remove sulphate. This can be due to the partial dissolution of formed ettringite, as the pH is close to the lower limit of ettringite stability range.

Additionally, the residual aluminium and calcium concentrations were measured as a function of pH (Figure 3). The residual aluminium and calcium concentrations were decreased by increasing pH from 11 to 12.5. This can be due to an increase in ettringite stability. At pH 12, the residual aluminium and calcium concentrations were less than 25 mg/L, and 140 mg/L, respectively. As calcium hydroxide and deionized water were added to ettringite in stoichiometric amounts, residual aluminium, calcium, and sulphate were present, due to ettringite solubility. Moreover, the ettringite yield increased with increasing pH by 82%, 86%, 87%, and 88% at pH 11, 11.5, 12, and 12.5, respectively.

X-ray diffractograms of the ettringite precipitates prepared with different pH were used to identify ettringite (ICDD 04-013-3691) and calcite (ICDD 04-066-0867) peaks at pH range 11.0–12.5 (Figure 4). The amounts of ettringite and calcite in the solid samples were determined using full-pattern quantitative Rietveld analysis. The precipitates contained 97%, 98%, 98%, and 96% ettringite at pH 11.0, 11.5, 12.0, and 12.5, respectively. The precipitates also contained 2%–4% calcite, which is common in ettringite precipitation, as calcium reacts with atmospheric CO_2 dissolved in water, forming calcite. At pH 12.5, the precipitate contained more calcite than at pH 11.5, and 12.0. This could be due to an increase in CO_2 concentration in the water, as dissolution of CO_2 increases with increasing pH (Fang et al., 2018). High purity ettringite

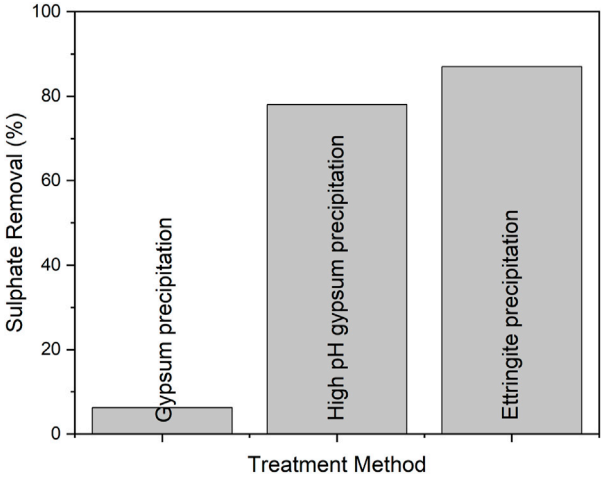

FIGURE 7
The percentage of sulphate removal from the industrial wastewater used in this study by gypsum and ettringite precipitations.

was attained in the ettringite precipitation experiment in all tested pH values.

3.3 Arsenic removal from synthetic wastewater

Arsenic removal by ettringite precipitation was examined using the synthetic wastewater solutions with initial sulphate concentration of 2,000 ppm and arsenic concentrations of 58 and 100 ppm. Figure 5 shows the percentage of arsenic and sulphate removal from the synthetic wastewater solutions. Sulphate removal decreased with increasing the initial arsenic concentration, which indicates that arsenic was replacing sulphate in ettringite structure. Additionally, the arsenate co-precipitation during ettringite synthesis was studied by Myneni et al. Myneni et al. (1998) using Fourier transform infrared (FTIR) and Raman spectroscopy. It was suggested that AsO_4^{3-} was preferentially substituted for SO_4^{2-} inside the channels at low sorption densities. The current results show that by increasing the initial arsenic concentration from 58 to 100 ppm, the percentage of arsenic removal decreased from 95% to 89%. This could be due to the fact that the surface sites available for substitution are being occupied, as the mass percentage of arsenic in precipitate containing 58 ppm arsenic was lower than that of precipitate containing 100 ppm arsenic (0.84% and 1.1%, respectively).

The precipitates were analysed using ICP-OES, XRD (Figure 6) and FESEM-EDS (see Figure A2). According to XRD and Rietveld analysis, the precipitates were above 98% ettringite, and the remaining was gypsum. The peak associated with arsenic oxide (As_4O_6 ICDD 01-084-7622) and ettringite (ICDD 04-013-3691) were observed at 31.7° and 31.9°, respectively (Figure 6). The peak intensity at 31.7° was relatively higher when the arsenic concentration in the synthetic wastewater solution was increased from 0 to 100 ppm. This observation is in agreement with ICP-OES measurements where arsenic concentration in the precipitate increased by 0, 25, and 34 mg/g with increasing the initial arsenic concentration in synthetic wastewater solutions (0, 58, and 100 ppm), respectively.

The FESEM-EDS analysis was conducted for the precipitates from arsenic co-precipitation experiments in both small rectangle area and point analysis and the results are summarized in Table 2. The ratio of Al:S was calculated in different points/areas. The current results show that the ettringite sample precipitated in absence of arsenic pentoxide had the Al:S ratio of approximately 2:3 in all analysed points, while the ettringite samples precipitated in the presence of 58 ppm arsenic, the Al:S ratio was above 2:3 in majority of the analysed points. This indicates that the arsenate ions could have replaced some of the sulphate ions in ettringite molecular structure. However, in some analysed points, the Al:S ratio was approximately 2:3, or even lower (e.g., points number 41 and 48, and area number 51). Lower Al:S ratio could be due to the heterogeneity of the sample as the precipitate also contains gypsum. The ettringite samples precipitated in the presence of 100 ppm arsenic, had the Al:S ratio of above 2:3 in majority of the analysed points. The Al:S ratio was also higher than that of the ettringite samples precipitated in the presence of 58 ppm arsenic, indicating the higher degree of sulphate substitution by arsenate. In point number 102, the Al:S ratio was the same as the ettringite stoichiometric ratio. In point number 107 and area 109, the Al:S ratio was lower, which can be due to the presence of gypsum in the precipitate. The current XRD and FESEM-EDS results demonstrate that the arsenic is removed both as arsenic oxide, and by substitution of sulphate ions in ettringite molecular structure by arsenate.

3.4 Sulphate removal from industrial wastewater

An industrial wastewater with high initial sulphate concentration (16,000 ppm) was used for sulphate removal using ettringite precipitation. The industrial wastewater was treated with gypsum precipitation in order to decrease its sulphate concentration prior to the ettringite precipitation, as sulphate concentration limit (lower than 2,000 ppm) would be useful for ettringite precipitation. The traditional gypsum precipitation at pH 9.5 resulted in only 6.3% sulphate removal with

TABLE 3 Properties of the sludge and the industrial wastewater after the gypsum and ettringite precipitation experiments.

Treatment/precipitation	Sulphate [mgL^{-1}]	Turbidity [NTU]	Sludge volume [ml]	Sludge dry mass [g]	Sludge solids content [g L^{-1}]	Sludge density [g L^{-1}]
None	16000	26.5	—	—	—	—
Gypsum	15000	10.1	196	1.6	8.3	1042
High pH gypsum	3300	7.3	614	23.3	38.0	1062
Ettringite	450	1.5	320	10.5	32.7	1102

residual sulphate concentration of 15,000 ppm. This is due to an insignificant dosage of calcium hydroxide needed to raise pH of the wastewater (initial pH 7.1 ± 0.3) to target pH 9.5, and to remove of more sulphate as gypsum. Additionally, the wastewater contained magnesium (concentration 2,500 ppm) which can disturb sulphate precipitation by keeping sulphate in the soluble form of magnesium sulphate, as shown in a previous study (Tolonen et al., 2015). Therefore, due to the fact that the sulphate concentration in the industrial wastewater was still above 2,000 ppm, a second gypsum precipitation was conducted as pre-treatment prior to the ettringite precipitation experiment. In this stage, calcium was added as calcium hydroxide in stoichiometric ratio (Ca:SO_4 1:1), which led to an increase in pH to 12.9. Following this high pH gypsum precipitation, the sulphate concentration decreased by 78.0%, leading to residual sulphate concentration of 3300 ppm. At pH 12.9, magnesium precipitated both as hydroxide and carbonate. The formed precipitate contained 86.7% gypsum, 3.3% magnesium hydroxide, 2.2% magnesium carbonate and 7.8% calcium carbonate. Magnesium concentration after high pH gypsum precipitation was less than 0.1 ppm.

The ettringite precipitation experiment was conducted using ye'elimite mineral, which further decreased the sulphate concentration in industrial wastewater by 87%–450 ppm. The percentage of sulphate removal after gypsum and ettringite precipitations are shown in Figure 7. The purity of formed ettringite was 99% determined by XRD and Rietveld analysis. Properties of the sludge and the industrial wastewater after the gypsum and ettringite precipitation experiments are shown in Table 3. Formed ettringite is stable as material.

4 Conclusion and recommendations

The suitability of Ye'elimite mineral as an alternative aluminium reagent to form ettringite precipitate from sulphate and arsenic containing synthetic wastewater and industrial wastewater solutions was examined. The title study showed that sulphate removal of up to 98% from the synthetic wastewater and 87% from the industrial wastewater can be achieved using ye'elimite as the aluminium source in the ettringite precipitation. The purity of precipitated ettringite was high in both synthetic and industrial wastewaters. Additionally, up to 95% arsenic removal was achieved in arsenic co-precipitation experiments from the synthetic wastewater.

The current study demonstrated that ye'elimite mineral can be used as a novel alternative to aluminium salts for removal of sulphate and arsenic from wastewaters. Additionally, ye'elimite mineral contains calcium, which can also offer the advantage of decreasing the amount of calcium hydroxide required to be employed during the ettringite precipitation process.

In the current study, the ye'elimite dissolution process showed optimised performance when used in combination with hydrochloric acid; however, it is envisaged that ye'elimite sintering process (e.g., residence time, temperature, and cooling rate) and physical properties (e.g., particle size and morphology) can be adjusted to enhance the dissolution. Furthermore, ye'elimite can be doped with other elements, e.g., iron which can substitute aluminium in the ye'elimite structure and this may offer advantages for enhanced dissolution. For further fundamental investigations, the influence of any common ion and/or inhibition effects can be studied. Moreover, the remaining ettringite sludge can be blended and re-fired into ye'elimite to enable circularity, while the carbonation of ettringite sludge offers additional benefits (e.g., carbon capture) or other recycling routes for the ettringite sludge, in an age where resource efficiency is crucial.

The current work has shown that water treatment using cement clinker phases is possible. After all, cements are designed such that water/fluid-particle reaction processes lead to dissolution of a solid oxide and subsequent precipitation of minerals. This study has unlocked a gateway for the utilisation of cement clinker phases/

minerals in water treatment, such as those in the mayenite group which can form complex solid solutions.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

Author contributions

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Appendix A

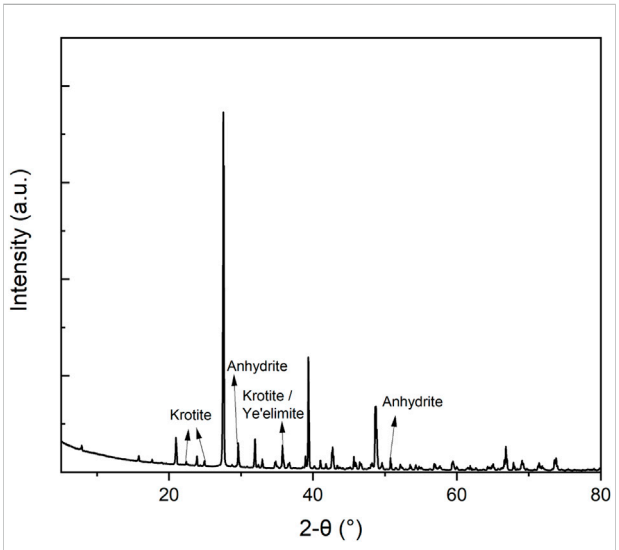

FIGURE A1
X-ray diffraction (XRD) pattern of the synthesized Ye'elimite used in this study. The unlabelled peaks refer to ye'elimite.

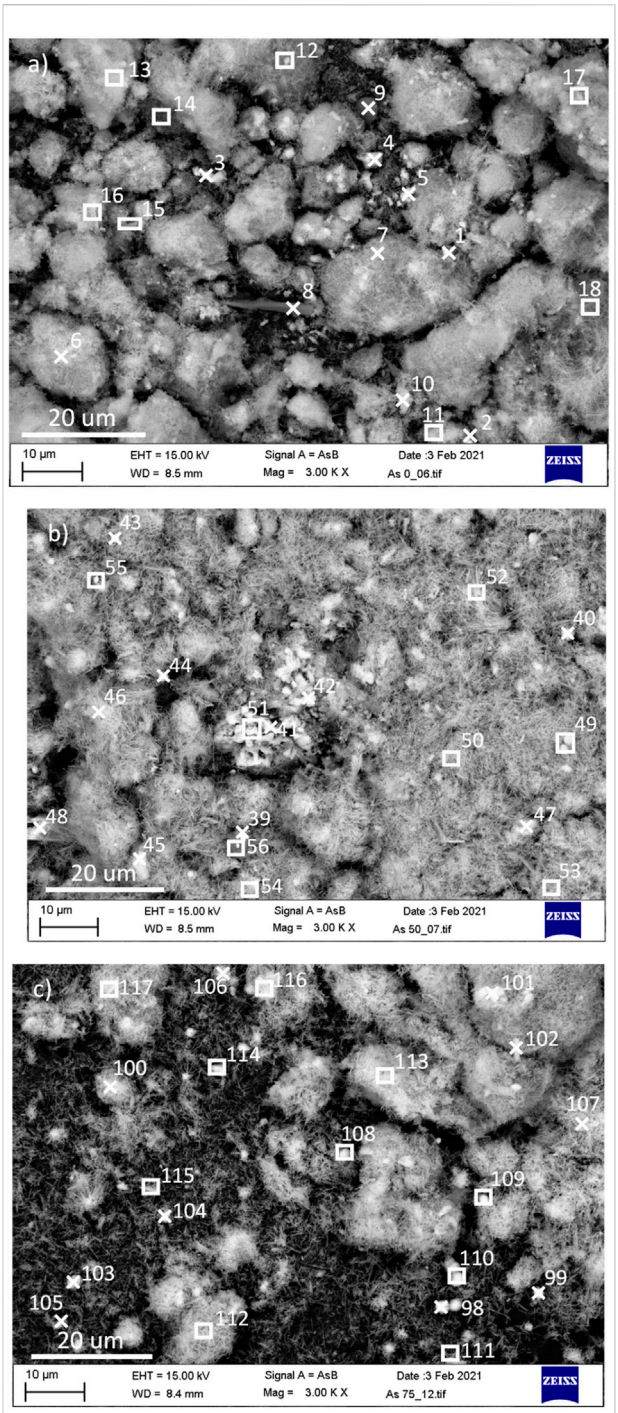

FIGURE A2
FESEM-EDS analysis of the precipitates synthesized **(A)** in the absence of arsenic, **(B)** in the presence of 58 mgL^{-1} arsenic, and **(C)** 100 mgL^{-1} arsenic.