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Efficient Inorganic ^{14}C Removal using Ettringite from Waste Solution

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Layout of presentation

- Introduction (why ettringite & ^{14}C?)
- Synthesis & characterization of ettringite
- Application of ettringite for sequestration of ^{12}C (non-radioactive surrogate of ^{14}C) from simulated waste solutions ($NaHCO_3$)
  - As HCO_3^- (at intermediate pH ~8.50)
  - As CO_3^{2-} (at high pH ~11.50)
- Desorption tests
- Conclusions

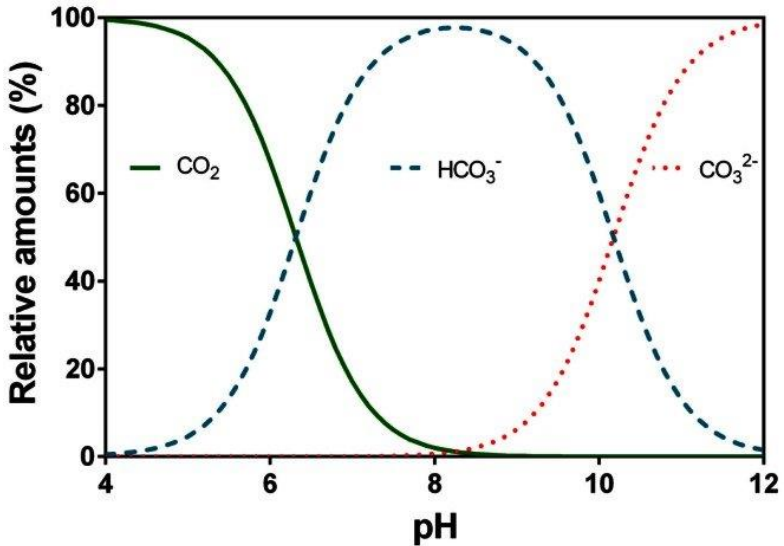
Why ettringite & ^{14}C ?

- Carbon-14 (^{14}C), a radionuclide generated in nuclear power plants and nuclear reactor operation, is a serious environmental threat due to its long half-life ($t_{1/2}$ = 5730 years) and potential mobility in the environment.

- A large quantity of ^{14}C is being produced in the reactor water (coolant and moderator), can be discharged from the nuclear facilities into rivers and/or seas and enhance the concentration of ^{14}C in the aqueous environment.

- Depending on the pH of the solution, the dissolved inorganic carbon can be distributed carbon dioxide ($CO_2(aq)$), bicarbonate (HCO_3^-), and carbonate ion (CO_3^{2-}).

- In alkaline aqueous media/waste solution, ^{14}C mainly exists as dissolved inorganic carbonate species (bicarbonate and carbonate).

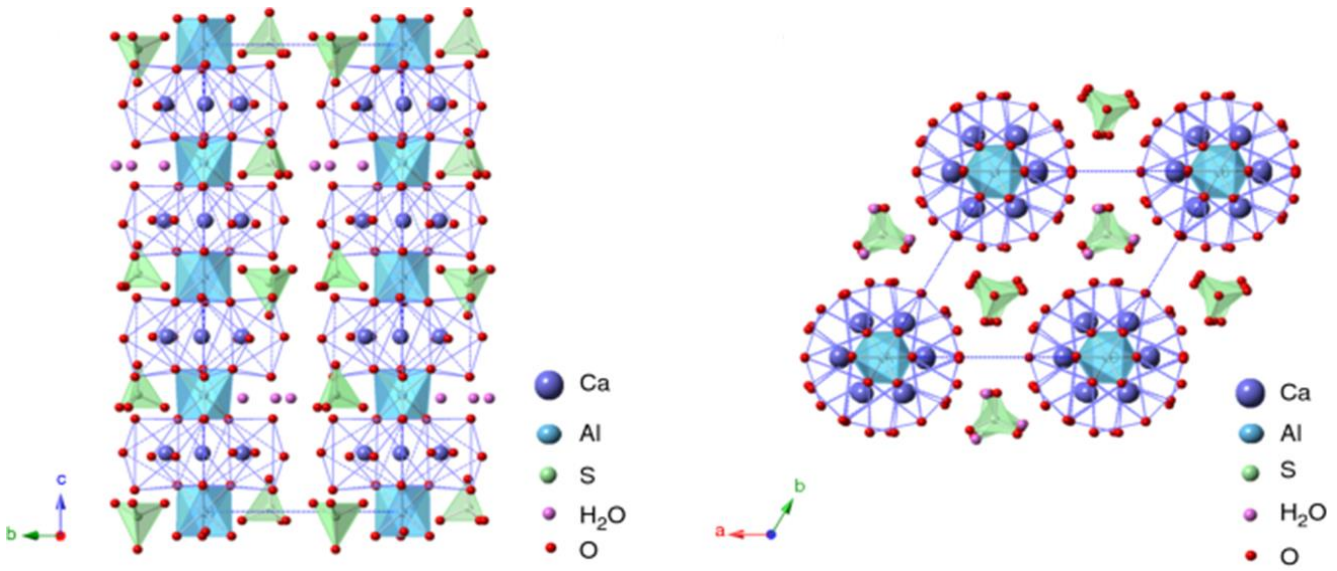


Ettringite

- Ettringite is a hydrous calcium aluminum sulfate naturally occurring mineral and a hydration product of Portland cement [$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$].

- J. Lehmann (in 1874) coined the term ettringite due to it occurrence near the Ettringer Volcano, Ettringen, Germany.

- It is known to immobilize anions via substituting a) TcO_4^- and IO_3^- for sulfate (SO_4^{2-})) from the channels as well as b) $AsO_4^{3-}$and SeO_3^{2-} for OH or H_2O from ettringite surface (≡Ca-OH_2, ≡Al-OH) or channel (≡Ca-OH_2) sites.



Synthesis of ettringite

Reagents/Chemicals: Calcium nitrate tetrahydrate [$Ca(NO_3)_2.4H_2O$], aluminum sulfate octadecahydrate [$Al_2(SO)_3.18H_2O$], sodium hydroxide (NaOH), and deionized water (DIW).

Deionized water (DIW) was boiled to remove dissolved CO_2 and cooled it down to room temperature (RT)

2.1255g $Ca(NO_3)_2.4H_2O$ + 150 mL DIW (**A**)

0.996g $Al_2(SO_4)_3.18H_2O$ + 150 mL DIW (**B**)

0.72g NaOH + 150 mL DIW (**C**)

- ✓ Solutions A and B were mixed and stirred for ~10 minutes at RT
- ✓ Solution C was poured into the resultant mixture and was stirred for 5 minutes at RT

Final mixture was kept overnight at RT in a static mode

The precipitate was vacuum filtered and washed with NH_3 (aq) ammonia 5 times

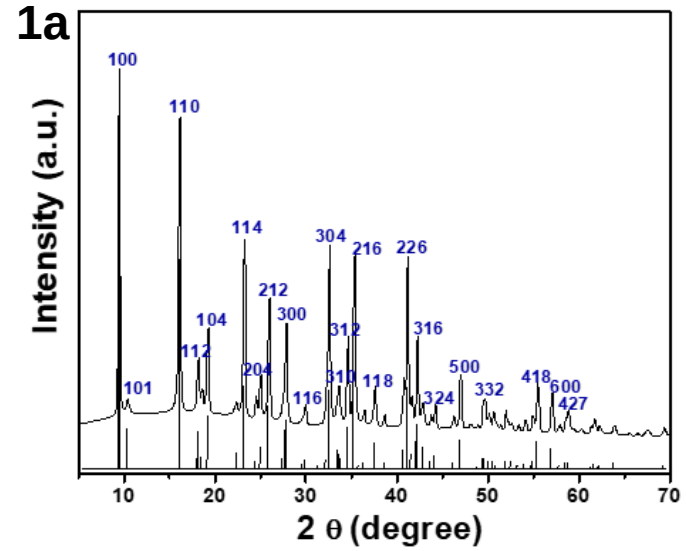
The washed solid was collected

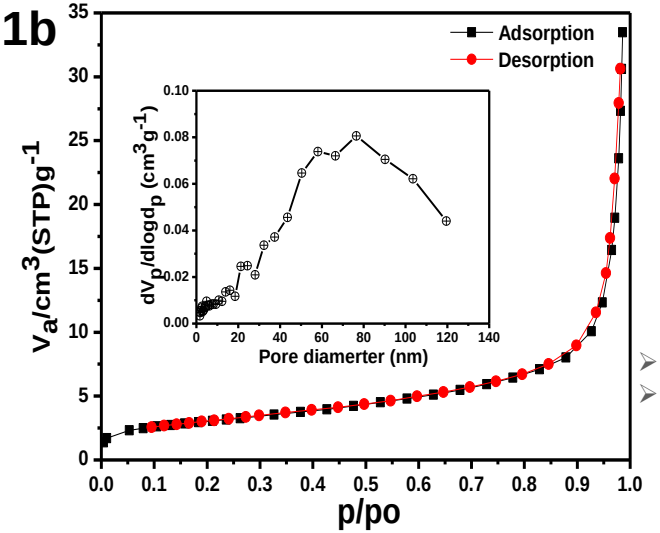
Dried in an oven at 40°C for overnight

Next day, the dried powder was obtained

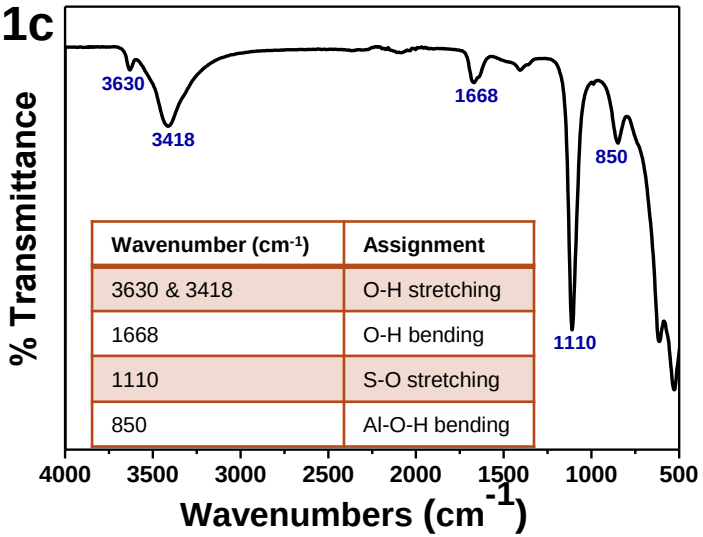
Synthesized Ettringite

Characterization of synthesized ettringite





- S_{BET} = 10.75 m^2/g
- Pore diameter = 50.94 nm



Wavenumber (cm^{-1})	Assignment
3630 & 3418	O-H stretching
1668	O-H bending
1110	S-O stretching
850	Al-O-H bending

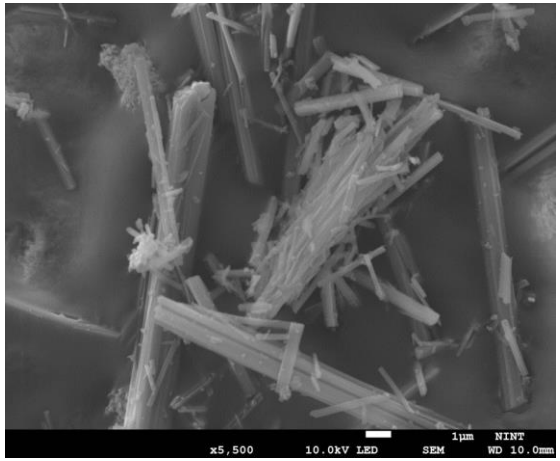


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Figure 1. Characteristics of synthesized ettringite. (a) Wide-angle X-ray diffraction (XRD) pattern of material with major reflections at their corresponding 2Θ values. (b) N_2 adsorption/desorption isotherms and BJH pore size distribution (inset Figure) data. (c) The FT-IR spectrum. (d) FE-SEM image.

Sequestration of HCO_3^-/CO_3^{2-} from simulated waste solutions

- Experiments were performed in polypropylene tubes (PPT) using simulated waste solutions (100 ppm $NaHCO_3$ in DIW; except the change in conc. of simulated waste samples).

    I. At intermediate pH (8.50), the existing species will be HCO_3^-
    II. Whereas, CO_3^{2-} species will dominate at high pH (11.50)

- Solid to waste solution ratio = 2 g/L and the samples were kept under dynamic condition using benchtop shaker (speed: 150 rpm) at RT.

- Various parameters, including contact times (kinetics) and concentrations of solid/ettringite and waste solutions were varied.

- Reaction time:10 m, 30 m, 1 h, 2 h, 4 h, 8 h, 12 h, 24 h, 48 h, 60 h, and 72 h.

- Pseudo first and second order kinetic modelling.

- Initial concentrations of HCO_3^- and CO_3^{2-} anions were varied as 36 ppm, 72 ppm, 108 ppm, 144 ppm, 180 ppm, and 216 ppm.

- Freundlich sorption isotherm analysis.

Sequestration of CO_3^{2-} from simulated waste solution

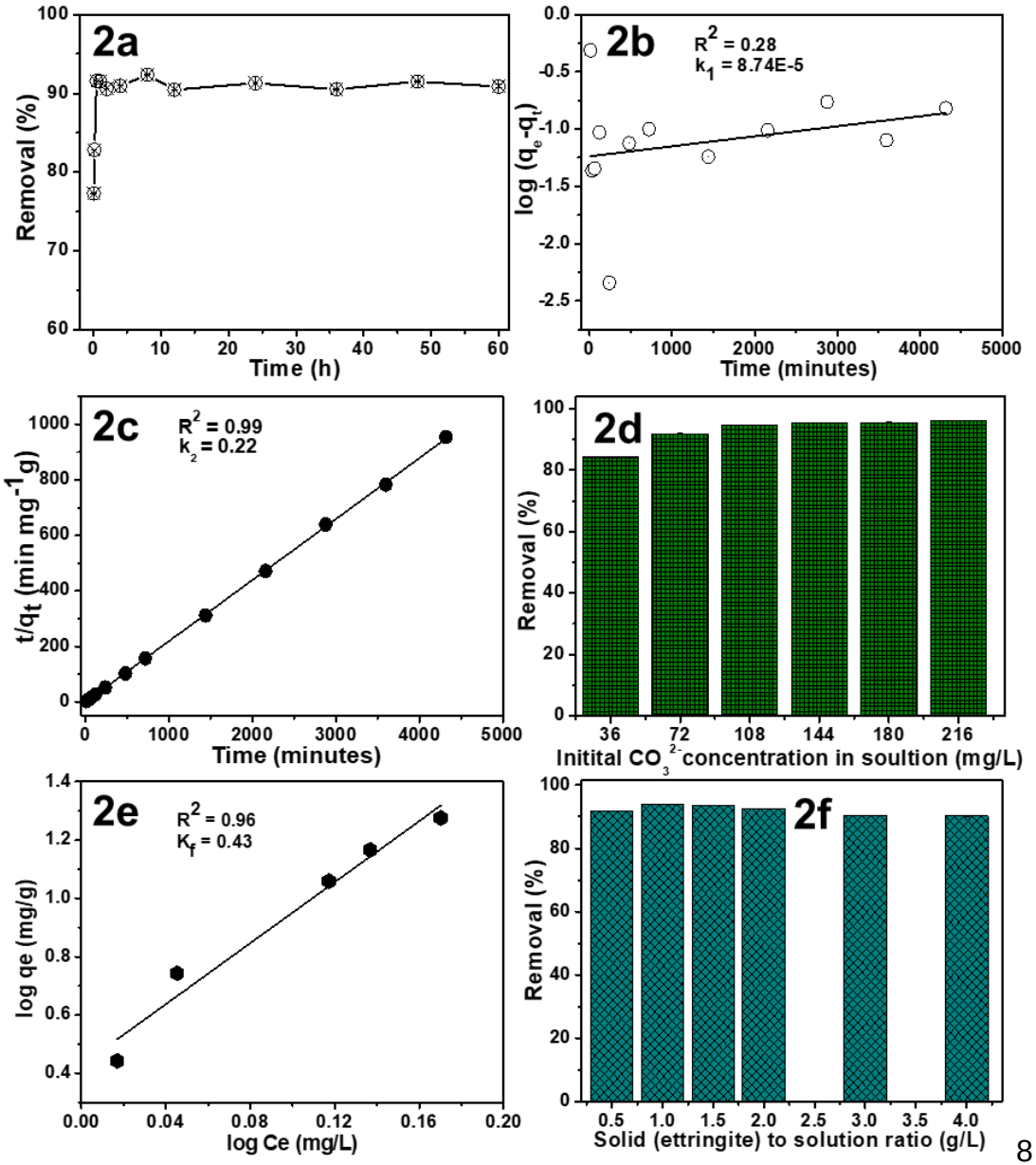
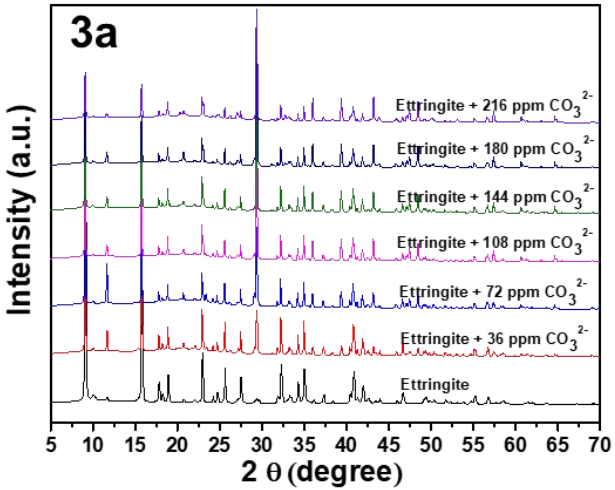
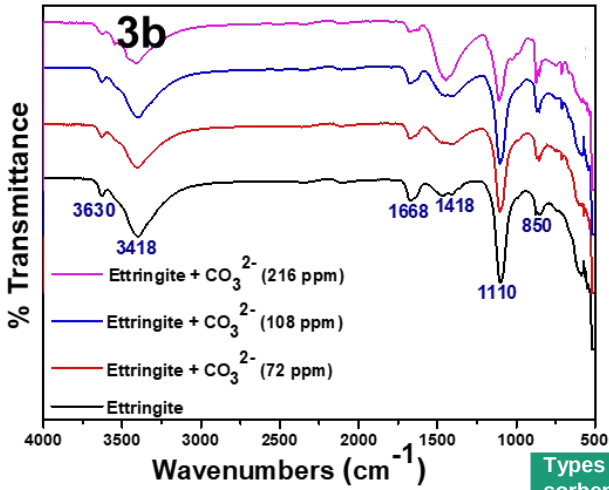


Figure 2. Sequestration of CO_3^{2-} anions from simulated waste solution using ettringite at high pH (~11.50) condition. (a) Kinetics of CO_3^{2-} anions removal [CO_3^{2-} anions = 72 ppm; S/L = 2 g/L; contact time = 5 m - 60 h] (b) Pseudo-first-order kinetic model for removal of CO_3^{2-} anions. (c) Applicability of pseudo-second-order kinetic model for removal of CO_3^{2-} anions. (d) Effect of initial CO_3^{2-} concentration in waste solution [CO_3^{2-} anions = 36 ppm - 216 ppm; S/L = 2 g/L; contact time = 8 h]. (e) Freundlich sorption isotherm analysis for removal of CO_3^{2-} anions. (f) Effect of sorbent concentration on CO_3^{2-} removal [CO_3^{2-} anions = 72 ppm; S/L = 0.5 g/L – 4.0 g/L; contact time =8 h].

Mechanism of CO_3^{2-} anions sequestration using ettringite





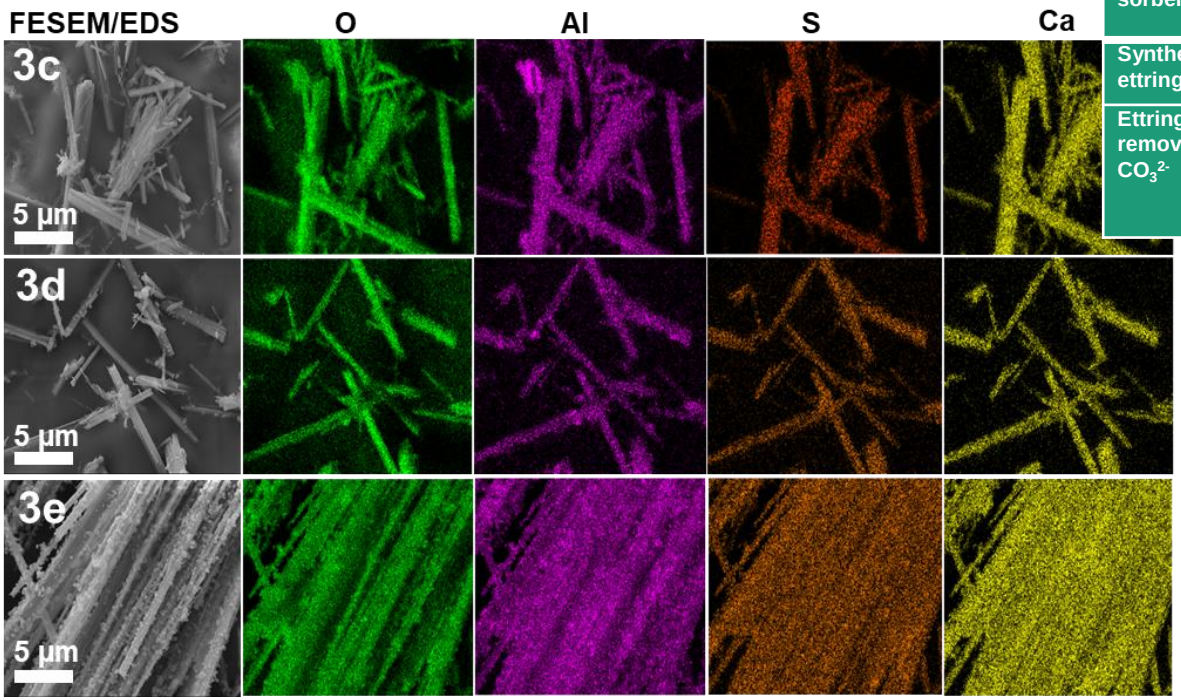


Figure 3. (a) Combined XRD plots for ettringite prior (black curve) and after removal of CO_3^{2-} anions (colored curves) at high pH (11.50) and different initial CO_3^{2-} concentrations (36 ppm-216 ppm) in simulated waste solutions. (b) The FT-IR spectra of ettringite (black) and after sequestration of CO_3^{2-} anions (colored data) anions at 72 ppm and 216 ppm initial concentration of CO_3^{2-} anions in simulated waste solutions, respectively.

Types of sorbent	Initial concentration of anions in sequestration experiments	S content (Wt. %)
Synthesized ettringite	NIL	6.84
Ettringite after removal of CO_3^{2-}	72 ppm initial concentration of CO_3^{2-}	6.71
	216 ppm initial concentration of CO_3^{2-}	7.06

Wavenumber (cm^{-1})	Assignment
1418	C-O stretching
1668	O-H bending
1110	S-O stretching
850	Al-O-H bending

Sequestration of HCO_3^- from simulated waste solution

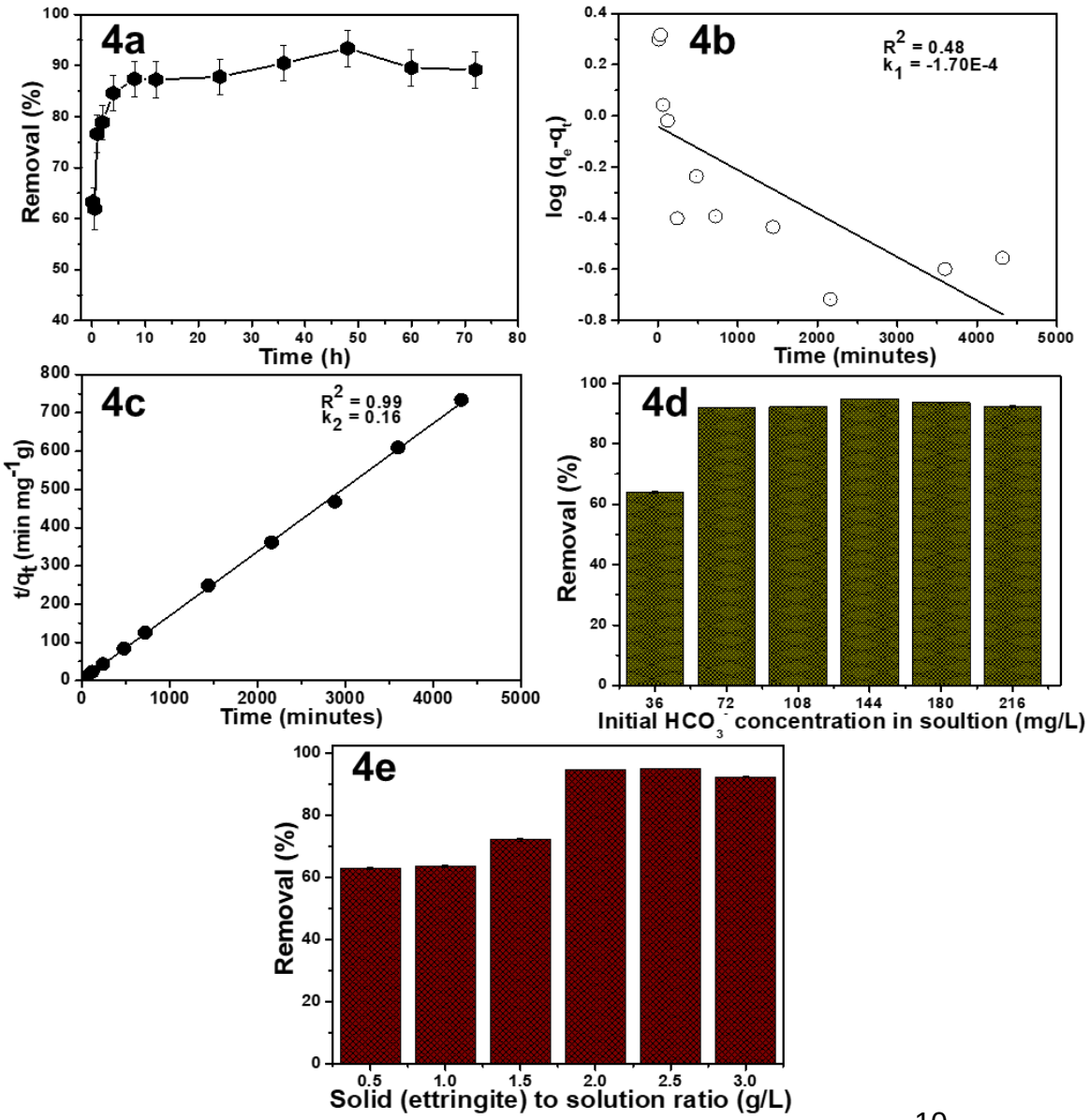
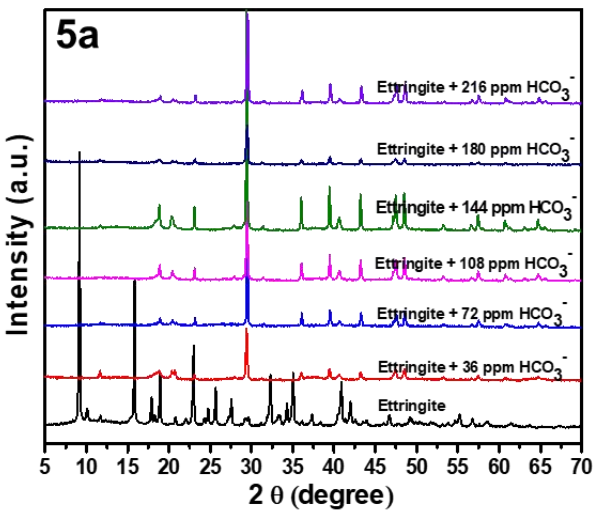


Figure 4. Sequestration of HCO_3^- anions using ettringite from simulated waste solution at intermediate pH (~8.50). (a) Kinetics of HCO_3^- anions removal [HCO_3^- anions = 72 ppm; S/L = 2 g/L; contact time = 10 m - 72 h] (b) Pseudo-first-order kinetic model for removal of HCO_3^- anions. (c) Pseudo-second-order kinetic model for sequestration of HCO_3^- anions. (d) Effect of initial HCO_3^- concentration in waste solution [HCO_3^- anions = 36 ppm -216 ppm; S/L = 2 g/L; contact time = 48 h]. (e) Effect of sorbent concentration on HCO_3^- removal [HCO_3^- anions = 72 ppm; S/L = 0.5 g/L – 3.0 g/L; contact time = 48 h].

Mechanism of HCO_3^- anions sequestration using ettringite



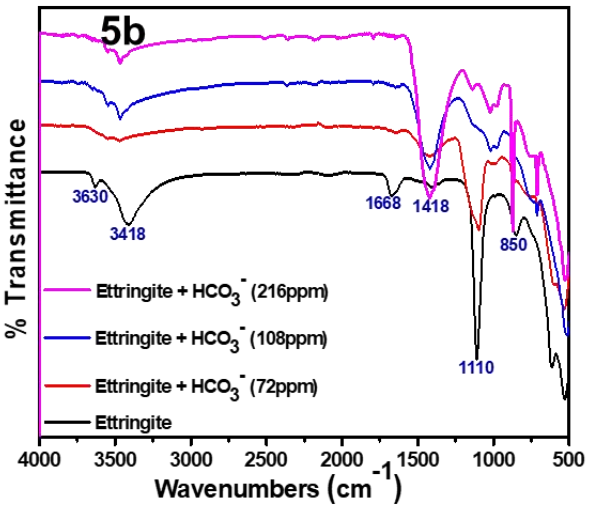
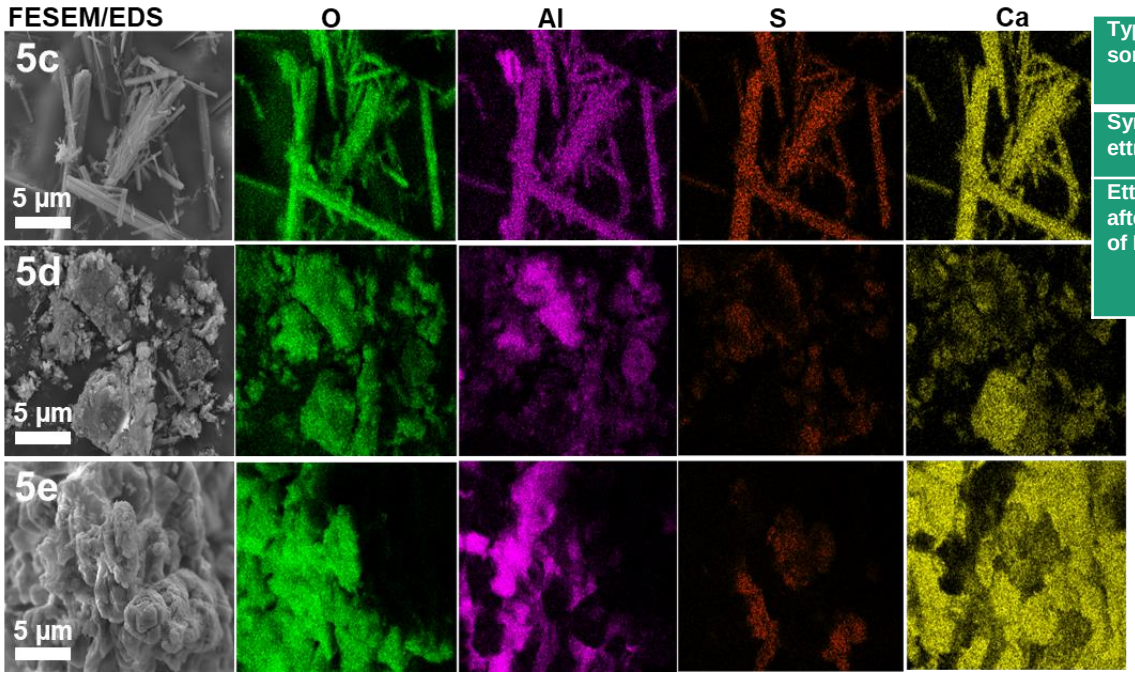


Figure 5. (a) The XRD patterns of ettringite prior (black data) and after removal of HCO_3^- anions (colored curves) at 36 ppm-216 ppm initial HCO_3^- concentrations in simulated waste solutions at intermediate pH (8.50). (b) The combined FT-IR spectra of ettringite (black) and after removal of HCO_3^- anions (colored data) at different initial HCO_3^- anions concentrations. (c) The FE-SEM image and EDS elemental mapping of synthesized waste solutions.

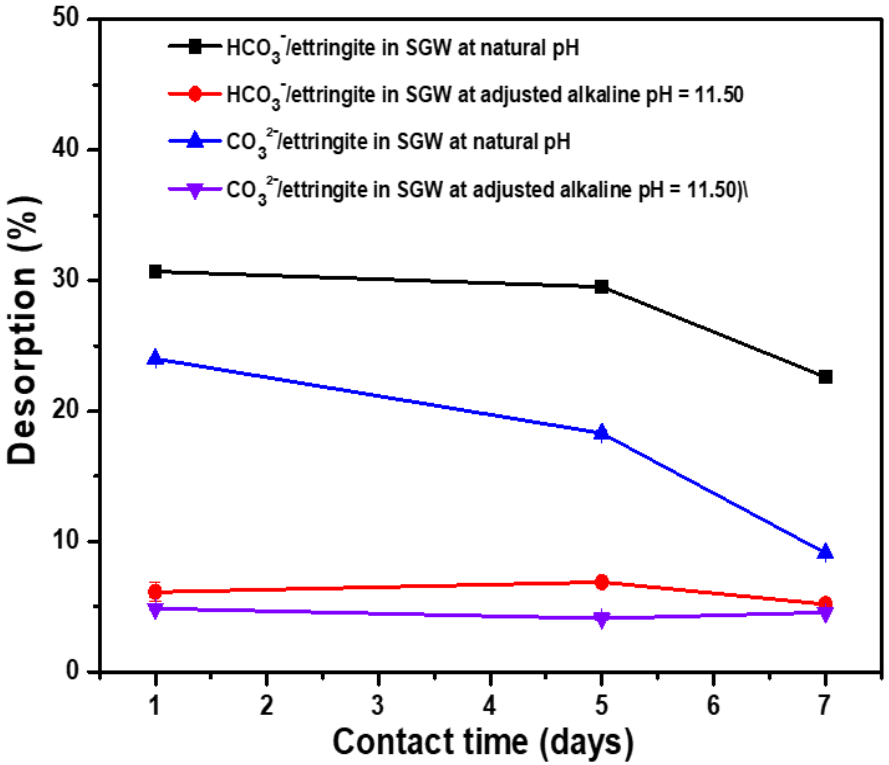


Types of sorbent	Initial concentration of anions in sequestration experiments	S content (Wt. %)
Synthesized ettringite	NIL	6.84
Ettringite after removal of HCO_3^-	72 ppm initial concentration of HCO_3^-	2.43
	216 ppm initial concentration of HCO_3^-	0.95

Wavenumber (cm^{-1})	Assignment
1418	C-O stretching
1668	O-H bending
1110	S-O stretching
850	Al-O-H bending

Desorption tests

- Desorption behavior of CO_3^{2-} and HCO_3^- anions from ettringite in simulated groundwater (SGW).
- Two sets of desorption experiments were performed in SGW condition both at its natural pH (~ 9.00) and adjusted pH (~ 11.50).
- SGW = 100 ppm $NaNO_3$, 100 ppm KCl, 100 ppm Na_2SO_4, and 50 ppm Na_3PO_4 in DIW
- Solid to solution ratio (ettringite to DIW) = 2g/L; Contact time 1 to 7 days.
- Samples were tested under dynamic condition using benchtop shaker (speed: 150 rpm) at RT.
- Desorption data were calculated in terms of desorption (%) and retention capacity (%).



Conclusions

- Characterization results (XRD, SEM, and FT-IR) confirmed the synthesis of highly crystalline homogeneous ettringite.

- Synthesized ettringite was used for the sequestration of carbonate anions both at intermediate and high pH conditions at RT.

- Obtained results revealed ~ 92-94 % sequestration of ^{12}C (surrogate of ^{14}C) from simulated waste solutions onto ettringite was achieved in 48 h and 8h at intermediate pH (~8.5) and high pH (~11.50), respectively.

- FESEM-EDS analysis and XRD results indicated a considerable phase alteration of ettringite at intermediate pH (HCO_3^-) removal tests. However, the ettringite structure was quite stable at high pH (CO_3^{2-}) removal experiments.

- Pseudo second order kinetic and Freundlich isotherm model was applied for the removal of carbonate anions onto ettringite.

- Ettringite demonstrated efficient CO_3^{2-} and HCO_3^- sequestration from simulated waste solution via ligand exchange, substituting OH/H_2O and SO_4^{2-} species from ettringite, respectively.

- Desorption results (retention capacity) suggested that the synthesized ettringite can be potentially applied for removal of ^{14}C from waste solutions both at the intermediate and high pH conditions.

I sincerely appreciate your attention

Any Questions ?