Transforming Methyl methacrylate via base-catalyzed hydrolysis

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Remediation of Chlorinated and Recalcitrant Compounds
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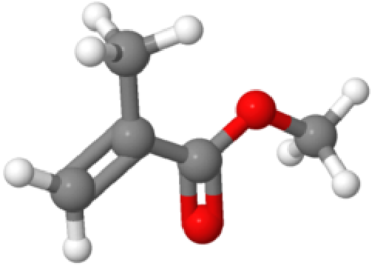
ISOTEC REMEDIATION TECHNOLOGIES

background

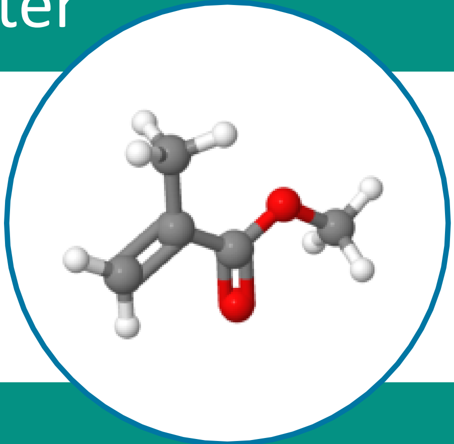
- MMA a colorless liquid with variety of uses, esp. mfg. acrylic plastics.
  - Perspex
  - Acrylite
  - Plexiglas
- Transported in bulk (tanker, bulk tote, e.g.)
- Potential for accidental acute release to environment



Methyl methacrylate (MMA)

- Volatile
- Very soluble in water
- Tends to sorb to soil

MMA (an Ester) Hydrolysis – Reaction with water



- pH 7 – ½ life 4 years
- pH 8 – ½ life 140 days
- pH 9 – ½ life 14 days
- pH 11 – ½ life 3.4 hours

Alkaline Hydrolysis – Ester

- Saponification

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR + NaOH\,(aq) \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-ONa\,(aq) + ROH$$

An ester | A base | A carboxylate salt | An alcohol

Alkaline hydrolysis of Esters

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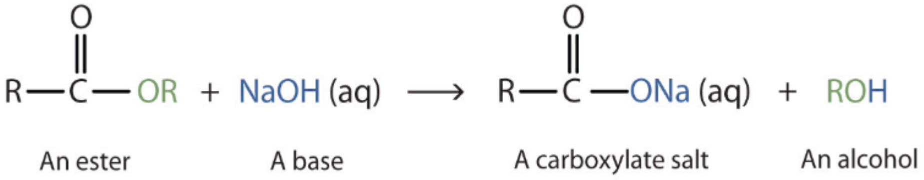
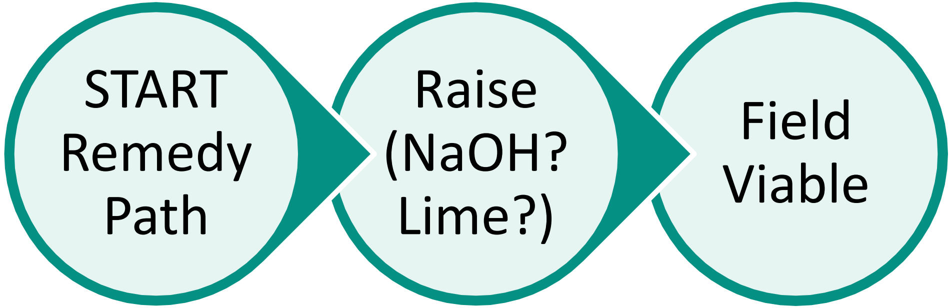
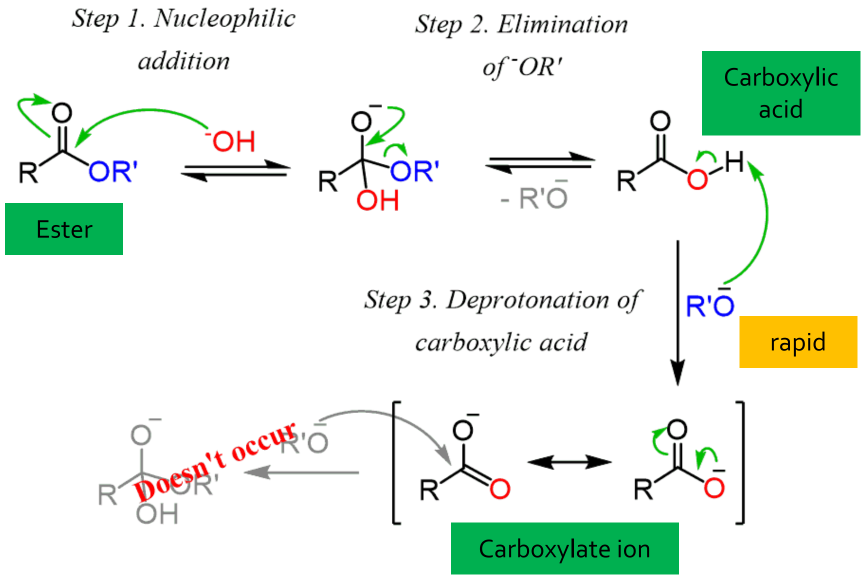




Mechanism of Base-Catalyzed Esters Hydrolysis



Step 3 makes ***base-catalyzed ester hydrolysis irreversible*** since the carboxylate ion can no longer be attacked by a nucleophile

Natural In-Situ Processes Hint Treatment

OBSERVED In Situ

- Methanol (MeOH) present in-situ post release
- MeOH concentrations in soil exceed TCLP criteria by 20x

CONCLUDED

- Suggests MMA is breaking down via aqueous hydrolysis
- Need remedy to address MMA and MeOH (generated)
- Promote to bench study

AS RECEIVED at TREATABILITY LAB

- Soil: 500 mg/kg MMA; near 50 mg/kg MeOH
- GW: 120 ug/L MMA; near 5,000 ug/L MeOH

Bench Approach

Phase 1: Soil Buffer Capacity (NaOH)

- Determine amount base to raise & maintain soil alkalinity

Phase 2 - Step 1: Alkaline Hydrolysis Effect

- Evaluate 3 pH values over 3 – 5 days
- Analyze MMA & MeOH
- Promote pH to Ph 2 - Step 2

Phase 2 – Step 2: COC-treatment

- Treatment train
- Alkaline hydrolysis (MMA)
- Oxidation (MeOH)

Bench Approach – Reagent Selection

Used widely in field to create high pH condition

NaOH – Representative Base

Stabilized H_2O_2

circum-neutral pH organometallic complex (chelated iron) catalyst

Modified Fenton's Reagent (MFR)

Elevated pH achieved with lime or sodium hydroxide in field

Alkaline activated sodium persulfate

Phase 2 – Step 1 setup

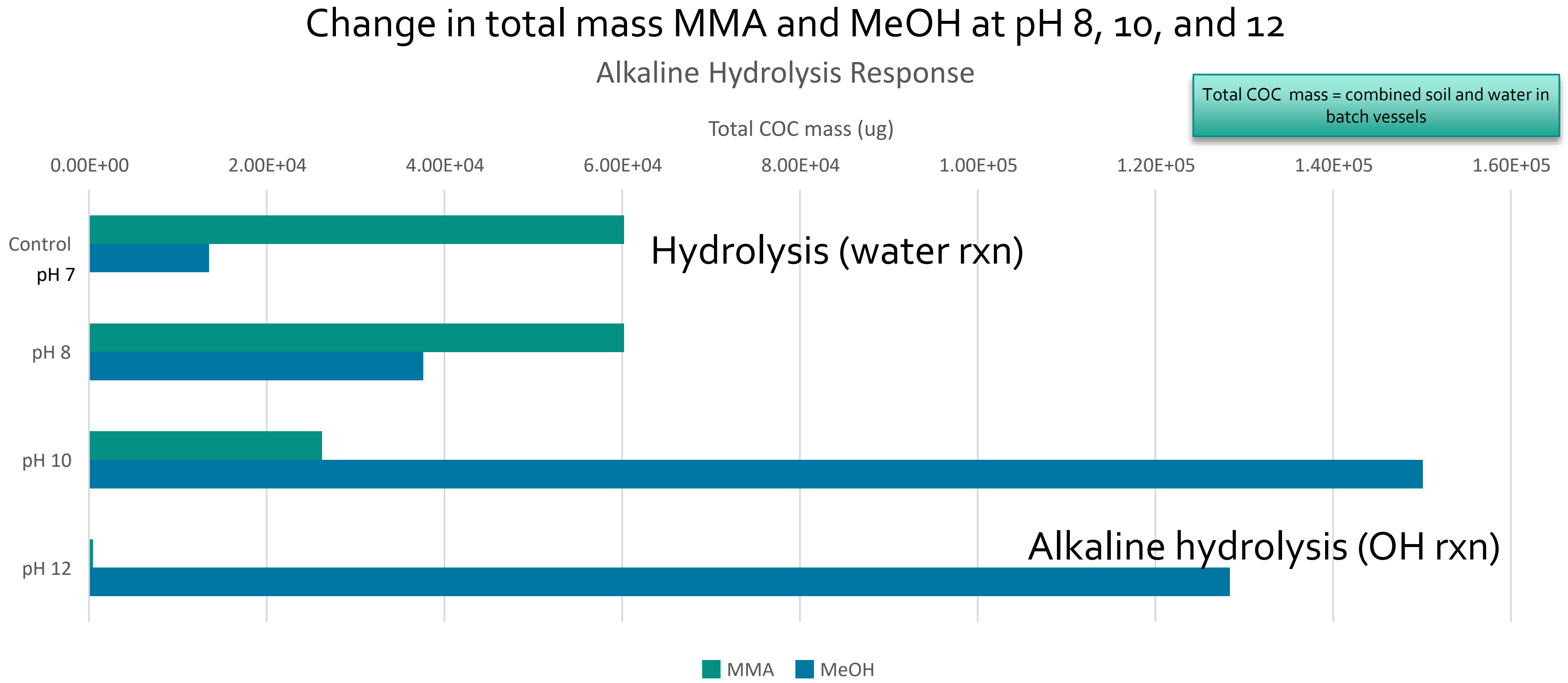
	Control	pH 8	pH 10	pH 12
Alkali added	None	NaOH		
Sample Time	Baseline & Final	Final	Final	Final
Analyze (soil and gw)	MMA & MeOH	MMA & MeOH	MMA & MeOH	MMA & MeOH

Results Phase 2 – step 1

Observed Change in Concentration (relative to Control) by Matrix

Relative Change in Concentration / Mass	pH=8		pH=10		pH=12	
MMA Conc. - aqueous phase	+	220%	+	53%	-	> 99.9%
MMA Conc. - solid phase	-	61%	-	87%	-	99%
MeOH Conc. - aqueous phase	+	355%	+	2093%	+	1043%
MeOH Conc. - solid phase	+	42%	+	177%	+	702%

Results Phase 2 – step 1

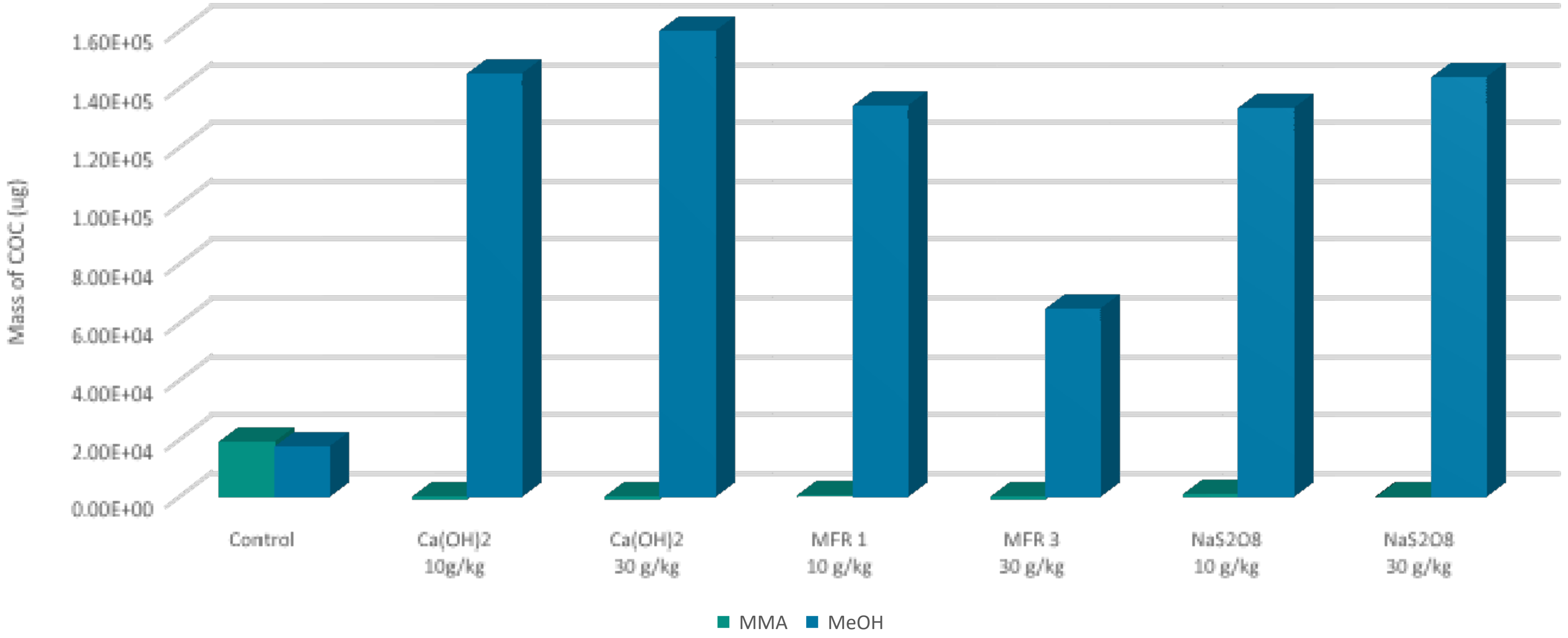


Phase 2 – Step 2 Setup

	COC Baseline & COC Control	Condition 2a	Condition 2b (Persulfate)	
		AH +MFR	CaSP	NaSP
Alkaline Hydrolysis (Day 0 - Day 2)				
Alkali used	none	NaOH	$Ca(OH)_2$	NaOH
Target pH value	ambient	pH= 11-12	pH= 11-12	pH= 11-12
Chemical Oxidation (Day 3 - Day 6)				
Oxidant used	none	H_2O_2	$Na_2S_2O_8$	$Na_2S_2O_8$
Doses tested	0 g/kg	10 g/kg, 30 g/kg	10 g/kg, 30 g/kg	10 g/kg, 30 g/kg
Parameter analyzed	VOCs (including MMA), MeOH			

Note: Based on AH-test results, a pH value between 11 and 12 was selected to be used in the test.

Phase 2 – Step 2 Results



Conclusions

- Recommend field treat with an alkaline reagent
  - Confirmed MMA transformed at pH>10
  - Lime or sodium hydroxide flake can be applied in an open pit scenario, e.g.
  - Liquid sodium hydroxide permeation injectable
- Methanol – manage aggressively
  - Assume field effort will require multiple oxidant treatments
  - Expect ketone (acetone, 2-butanone) generation
  - Slight risk: Persulfate decomposition product acting as catalyst for condensation rxn's – reform MMA?
- Oxidant efficiency
  - Completeness of oxidant consumption compared to the decrease in contaminant mass
  - MFR was most efficient oxidant on bench
  - Greatest change in MeOH concentration at 30g/kg MFR @ 95.8% oxidant consumption

Thank You

ISOTEC REMEDIATION TECHNOLOGIES

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