Permanganate for In Situ Chemical Oxidation of NDMA

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Outline

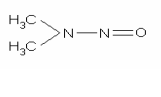
- Background
- Objectives
- Methods
- Summary of Experiments
- Results
- Recommendations
- Acknowledgments & Questions

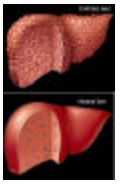
Background on Problem

- RCRA site N. of Boulder
- Raytheon Company, former Beechcraft site
- Manufacturing aerospace products
- Contaminated with:
  - Chromium
  - Trichloroethene (TCE)
  - Perchloroethence (PCE)
  - N-nitrosodimethylamine (NDMA)
- Cleanup options:
  - Bioremediation
  - Chemical Oxidation
    - Sodium Permanganate

Background on NDMA

- Emerging contaminant
  - State of CO clean-up target 0.69 ng/L (ppt)
- Yellow liquid, no distinct odor
- Found in:
  - In Rocket Fuel
  - Canned Food Products
  - Water & Wastewater disinfection
- Low partition coefficient
- Photo degrades in direct sunlight
- Inhalation by farm workers
- Medical Conditions:
  - Cancer, Cirrhosis, Jaundice, Vomiting, etc.





NDMA oxidation

- Chemical Oxidation
- Permanganate contains Manganate (VII) ion (MnO_4^-)
- Deep purple color
- Permanganate oxidation rate second order ove
  - chlorinated ethenes, MTBE, PAH's, PCE, TCE, TNT
- Theoretical NDMA breakdown stoichiometry:

$3\ C_2H_6N_2O + 22\ MnO_4^- + 22\ H^+ \ ?\ \ 6\ CO_2 + 6\ HNO_3 + 22\ MnO_2\ (s) + 17$
H2O NDMA Permangante Carbon Nitric
Manganese ion dioxide
Acid Dioxide

22 moles of MnO4- fully oxidize 3 moles NDMA (14 mg:1 mg = SR)?

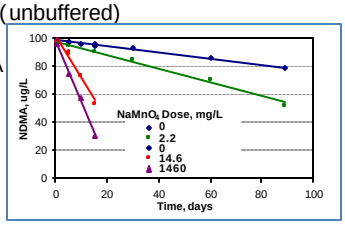
Reaction Kinetics

Oxidation rate of NDMA is related to MnO4-: $\frac{d[MnO_4]}{dt} = SR * \frac{d[NDMA]}{dt}$

- Zero order:
  - Reaction is independent of the concentration. $\frac{d[MnO_4]}{dt} = -k_0$
- First order:
  - Depends on the concentration of only one reactant $\frac{d[MnO_4]}{dt} = -k_1[MnO_4]$
- Second order: $\frac{d[MnO_4]}{dt} = -k_1[MnO_4][NDMA]$
  - Depends two first-order reactants.

Preliminary Experiments (by Rajat Srivastav)

- Oxidation of 100 µg/L NDMA by 0 – 10,000 mg/L commercial permanganate (RemOx)
  - Measured NDMA by GC/MS ($$$)
- Nanopure water (unbuffered)
- Methanol was present in NDMA spike



Experimental Objectives

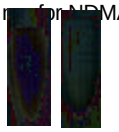
- Quantify the rate of NDMA oxidation via the permanganate consumption rate
  - In conditions closer to real groundwater (no MeOH, carbonate buffered system)
  - At different NDMA concentrations
  - Reagent grade permanganate vs. commercial RemOx
- Conduct Pretest:
  - Can a vial be sampled more than once?
  - Manganese dioxide interfere?

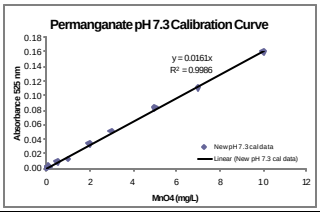
Methods

- Batch tests in amber glass vials
- Created stock solutions of Artificial Ground Water, MnO4, and NDMA
- Triplicates for varying concentrations, with multiple sets of vials to sacrifice over time
- Removed aqueous samples to quantify permanganate, NDMA, and pH

Methods

- Used spectrophotometer
- Created a calibration curve for permanganate
  - 525 nm measures permanganate
- 418 nm to confirm negligible MnO2(s) interference (centrifuged samples before measurement)
- 256 nm for NDMA



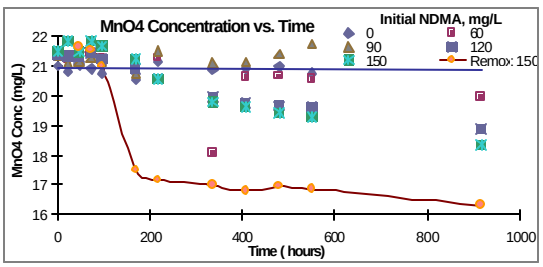


Pretest Summary

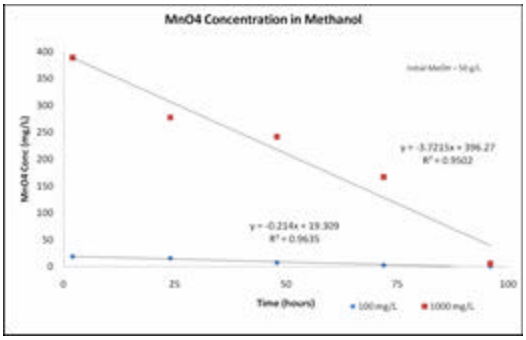
- Permanganate was quickly removed (<24 hrs) when methanol was present
  - Due to permanganate oxidizing the methanol
  - Initially 10 mg/L permanganate, ~50 g/L MeOH, and 0, 60, 150 mg/L NDMA
- Permanganate concentrations changed very slowly in systems with nanopure water (<2 mg/L loss in 21 days)
  - Initially 10 mg/L permanganate, and NDMA at 0, 60, and 150 mg/L

Test 1

- Data points represent average of triplicates
- 38 days: much less permanganate reduction than expected

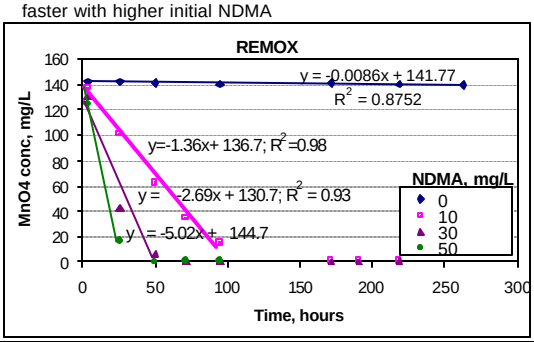


Test 1 cont …



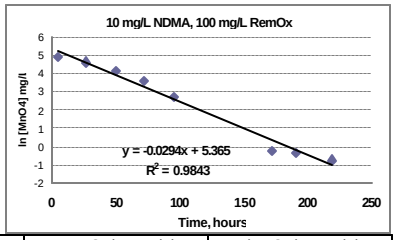
Final Test

- Initial permanganate removal rate zero order (as shown) and faster with higher initial NDMA



Final Test

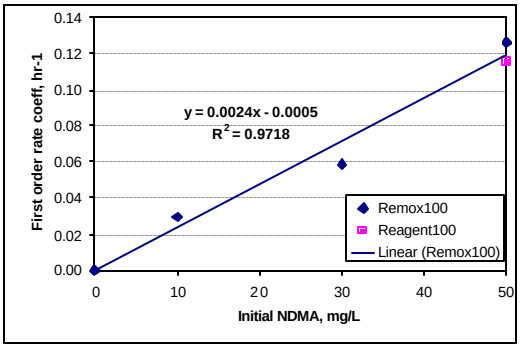
First Order Model fit Data……



Initial NDMA (mg/L)	Zero Order Model Time (hours)	R2	First Order Model R2	First Order Model Time (hours)
0	7	0.875	0.875	4-263 7
10	4-95 5	0.984	0.984	4-263 8
30	4-50 3	0.928	0.954	4-95 5
50	4-26	1	0.981	4-50 3

Only 2 data pts!

Second Order Overall



Decrease in NDMA ?

Some inaccuracy in previous approach if NDMA concentration changed significantly over time....

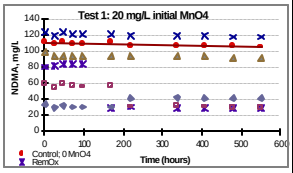
Main test no signif NDMA ?

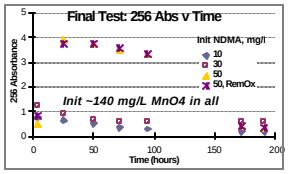
- Final Test NDMA conc. ??

Interference from:

- RemOx
- MnO_4

256 nm abs during with 0 NDMA & diff initial concs of RemOx or MnO_4





Stoichiometry

- Still working on . . .
  - Stoichiometry for permanganate consumption vs NDMA removal
  - Rajat's experiments with GC-MS measurement of NDMA are at ~134 mg MnO4-/mg NDMA (may be some oxidation of artificial groundwater inorganics occurring...?)

Final Test Stoichiometry		
NDMA, mg/L	**100 mg/L MnO4**	**Stoichiometry**
10	RemOx	113 mg MnO4/mg NDMA
30	RemOx	23 mg MnO4/mg NDMA
50	RemOx	13 mg MnO4/mg NDMA
50	RemOx (dilutedby5)	11.7 mg MnO4/ mg NDMA
50	Reagent	11.5 mg MnO4/mg NDMA

Summary of Results

- Permanganate oxidizes methanol very fast
- Higher concentrations of MnO4 oxidize NDMA faster than lower concentrations
  - First order rate with respect to MnO4
- Higher concentrations of NDMA reduce permanganate concentrations faster
  - First order rate with respect to NDMA
- RemOx oxidizes NDMA faster than reagent grade MnO4.

Further Work

- Why does RemOx work better than MnO4?
- Compare mg/L concentrations of NDMA to ug/L
  - Use to predict removal at ng/L (ppt) NDMA concentrations
    - Can clean-up limit of 0.69 ng/L can be achieved?
    - Or analysis of NDMA by a very high sensitivity method ($$$)
- Quantify the effects of varying natural conditions
- Determine stoichiometric reaction
  - Any toxic byproducts results?
  - GC/MS indicated some DMA formation (not yet quantified)

Acknowledgements and Questions

- Thanks to CU REU Program and Professors
- Dr. Bielefeldt
- Rajat Srivastav
- Amanda Kohler
- Grad students
- REU students

Questions ?