Bioremediation of Chlorate and Chromate Contaminated Groundwater in Cold Climate

Mehdi Motevasselin

Dr. Beata Gorczyca

Dr. Richard Sparling

Dr. Indra Kalinovich

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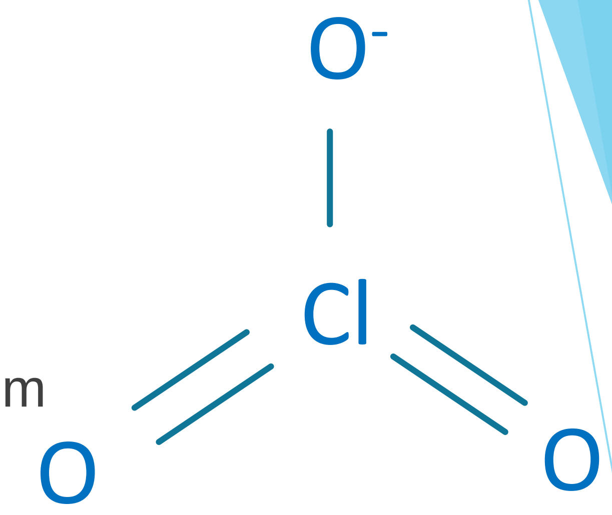
University of Manitoba

Background

Chlorate

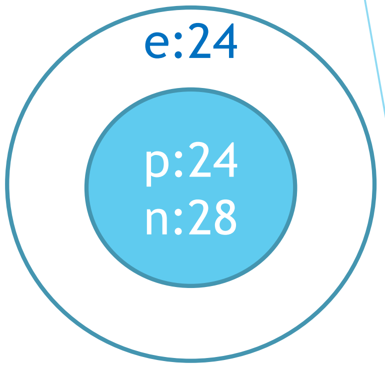
- As sodium chlorate, calcium chlorate, potassium chlorate, and magnesium chlorate
- Uses: Herbicide , Bleaching
- Health concerns: Blood, Thyroid
- Regulations: 1 mg/l in drinking water



Background

Chromate

- As chromium trioxide or chromic acid, potassium chromate, sodium chromate
- Uses: stainless steel, textile dyes, wood preservation, anti-corrosion, paint pigments
- Health concerns: respiratory tract, kidneys, eyes and skin
- Regulations: EPA: 0.1 mg/l , Canadian guideline 0.05 mg/L (50 µg/L) based on total chromium



$1S^2\ 2S^2 2P^6\ 3S^2 3P^6 3d^5\ 4S^1$

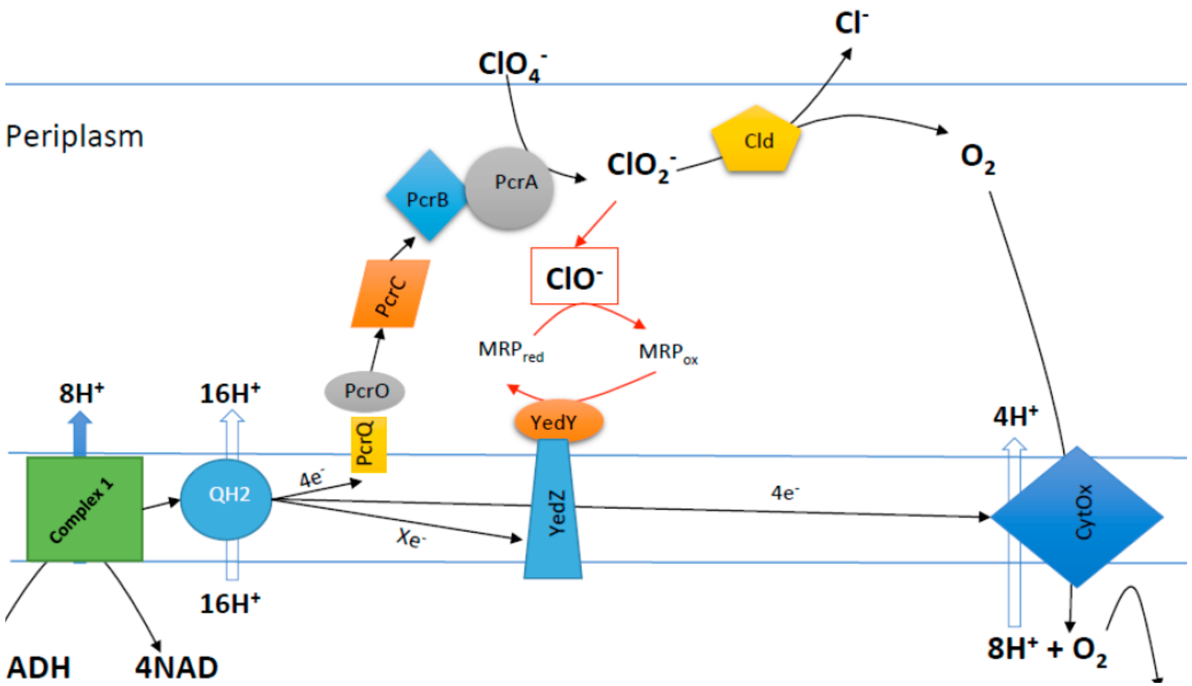
Background

Chlorine Ions Stability

Formula	Name	Oxidation state	Stability (aqueous phase)
Cl^-	chloride	-1	stable
ClO^-	hypochlorite	+1	unstable
ClO_2^-	chlorite	+3	unstable
ClO_3^-	chlorate	+5	stable
ClO_4^-	perchlorate	+7	very stable

Background

Perchlorate and Chlorate Bioremediation Path *



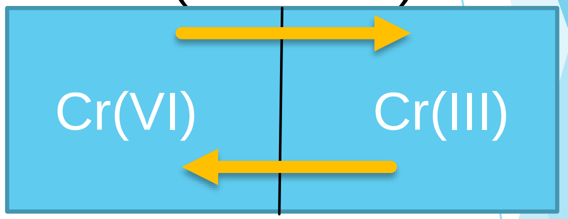
* Wang O., Coates John D., Biotechnological Applications of Microbial (Per)chlorate Reduction, open access article distributed under the terms and conditions of the Creative Commons Attribution

Background

Chromium Ions Stability

Formula	Oxidation state	Stability (aqueous phase)
Cr^{+}	+1	unstable
Cr^{2+}	+2	unstable
Cr^{3+}	+3	very stable
Cr^{4+}	+4	unstable
Cr^{6+}	+6	stable

Reduction
(e– donor)



Oxidation
(e– acceptor/ Bacteria)

Background

Bioremediation

- The only method is capable to remove contamination without any need to further processes, and with the minimum side effect on the environment
- In situ:
  - Natural
  - Engineered: Bio-stimulation, Bio-augmentation
- Ex situ

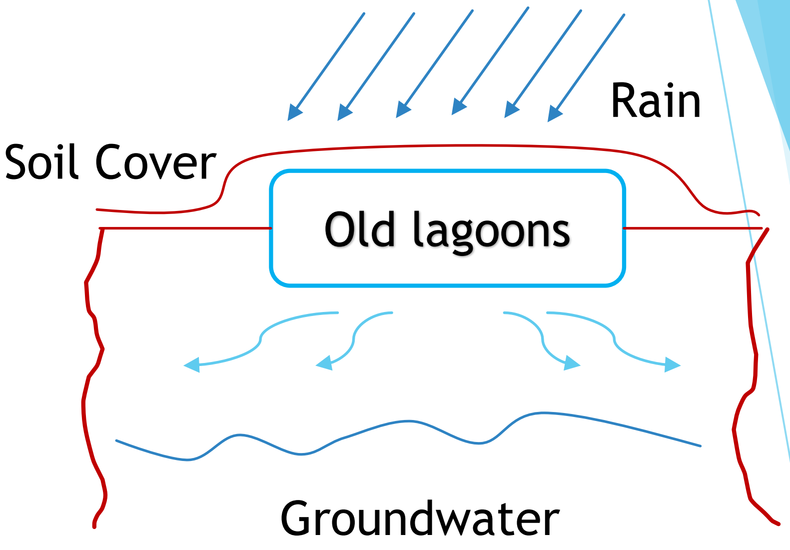
Background

Bioremediation

- Affecting Parameters:
  - Microorganisms
  - Bioavailability
  - Environmental circumstances: Substrate, Osmosis pressure, Contaminants solubility, Soil permeability, Oxygen, Temperature, pH, Moisture

Problem Statement

- Old lagoons were used to dump waste
- Chlorate: 3900 mg/l >> 1mg/l
- Chromium(VI): 3 mg/l > 0.05 mg/l



- Lack of proper electron donor prevented microorganisms from reducing chemicals
- Insufficient nutrients
- Absence of reducing bacteria

Objectives

- Determining the ability of microorganisms in the site to reduce chlorate and chromate to less harmful materials
- Specifying necessary nutrients for bioremediation
- Investigating the possibility of bioremediation process in cold conditions

Method

Synthetic Water

	Well data, groundwater		Synthetic media	
	(mg/L)	(mMol)		(mMol)
Chlorate	3900	46.71	Sodium chlorate (1000 mg/L chlorate)	11.97
Chromium(VI)	3.03	0.058	K_2CrO_4 (3 mg/L as Cr(VI))	0.058
Nitrogen (NO_3^-; NO_2^-)	15.9	NO_3^- 0.256 NO_2^- 0.346 Overall around 0.3		
Sulfate	672	9.73	0.1 g of $MgSO_4 . 7H_2O$	0.405
pH	7.25- 8.07		7.1-7.2	

Method

Nutrients and additives

	Well data, groundwater		Synthetic media	
	(mg/L)	(mMol)		(mMol)
Sodium acetate	-	-	2200 mg/l NaAcetate	37.262
Phosphorus and Nitrogen	4.16	0.134	500 mg/l $(NH_4)_2HP$	3.786
Minerals	-	-	ATCC 1191 1:100	

$$CH_3COO^- + 4/3\ CLO_3^- \longrightarrow 2HCO_3^- + H^+ + 4/3\ Cl^-\ {}^*$$

CNP molar ratio: 100:10:5

* G. B. Rikken et. Al Transformation of (per)chlorate into chloride by a newly isolated bacterium: reduction and dismutation, Appl Microbiol Biotechnol (1996) 45:420Ð426

Method

Batch Test Design

No.	Sample composition	Number of bottles
1 (C)	Synthetic water + Carbon source only (Acetate)	3
2 (C+M)	Synthetic water + Carbon source + Minerals (1:100)	3
3 (CNP)	Synthetic water + Carbon source + Nitrogen and Phosphorus	3
4 (CNP+M) Warm	Synthetic water + Carbon source + Nitrogen and Phosphorus + Minerals (1:100)	3
5 (CNP+M) Cold	Synthetic water + Carbon source + Nitrogen and Phosphorus + Minerals (1:100)	3

Method

Inoculum

- Wet soil contains 19% moisture
- Measuring enzymatic activity by FDA analysis showed that dry soil, wet soil and groundwater have 0.015, 0.016 and 0 mg/L Fluorescein concentration
- ATP analysis result for groundwater was 222.69 pg/L
- 4 gr of dry soil + 4 gr of wet soil + 2mL of groundwater for 400 mL of media (2.5% wt)

Method

Anerobic Condition

- All bottles degassed for 7 minutes and then purged with nitrogen gas for 3 minutes. This process has been done 4 times to make sure that all oxygen content has been removed.

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Method

Sampling

- Sampling were taken 3, 7, 14, 21,28, 35, 50, 58 , 80 days after starting the experiment
- HACH DR-3900 spectrophotometer was used for Cr(VI)
- IC machine for chlorate

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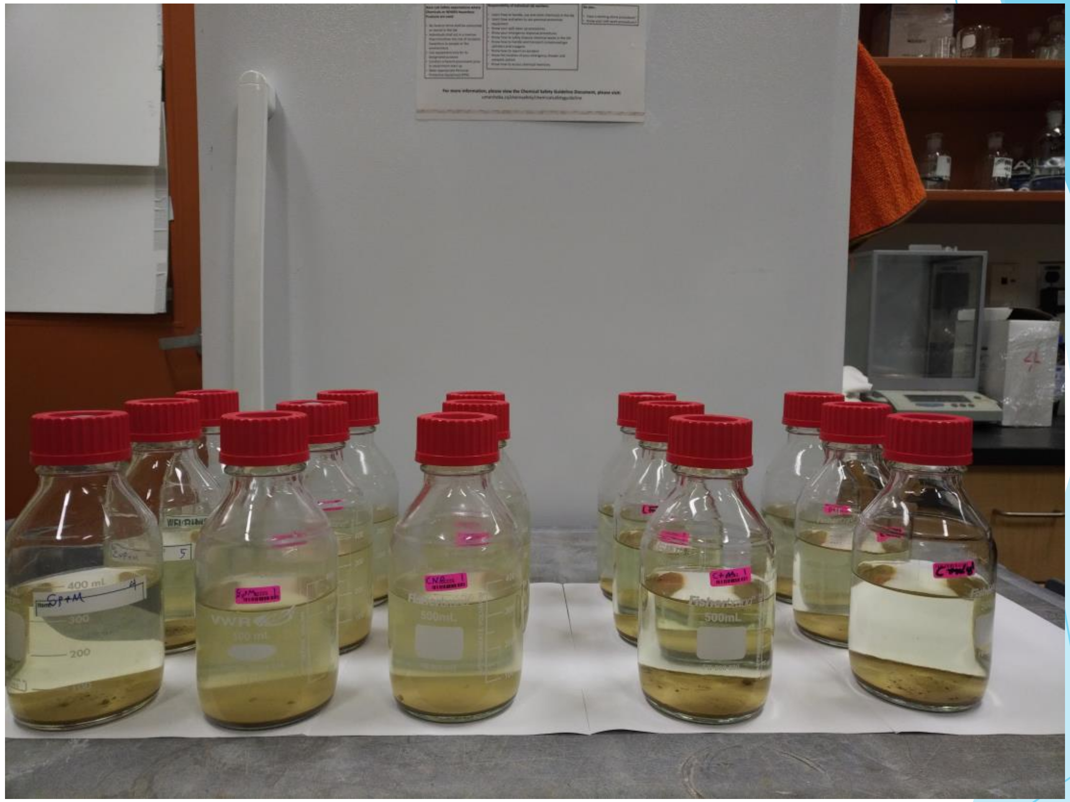
Results

Appearance after 5 weeks

- Samples without Nitrogen and Phosphorus source remained clear and transparent as well as bottles in the cold chamber in 10 ^{o}C while microcosms containing N and P became cloudy.



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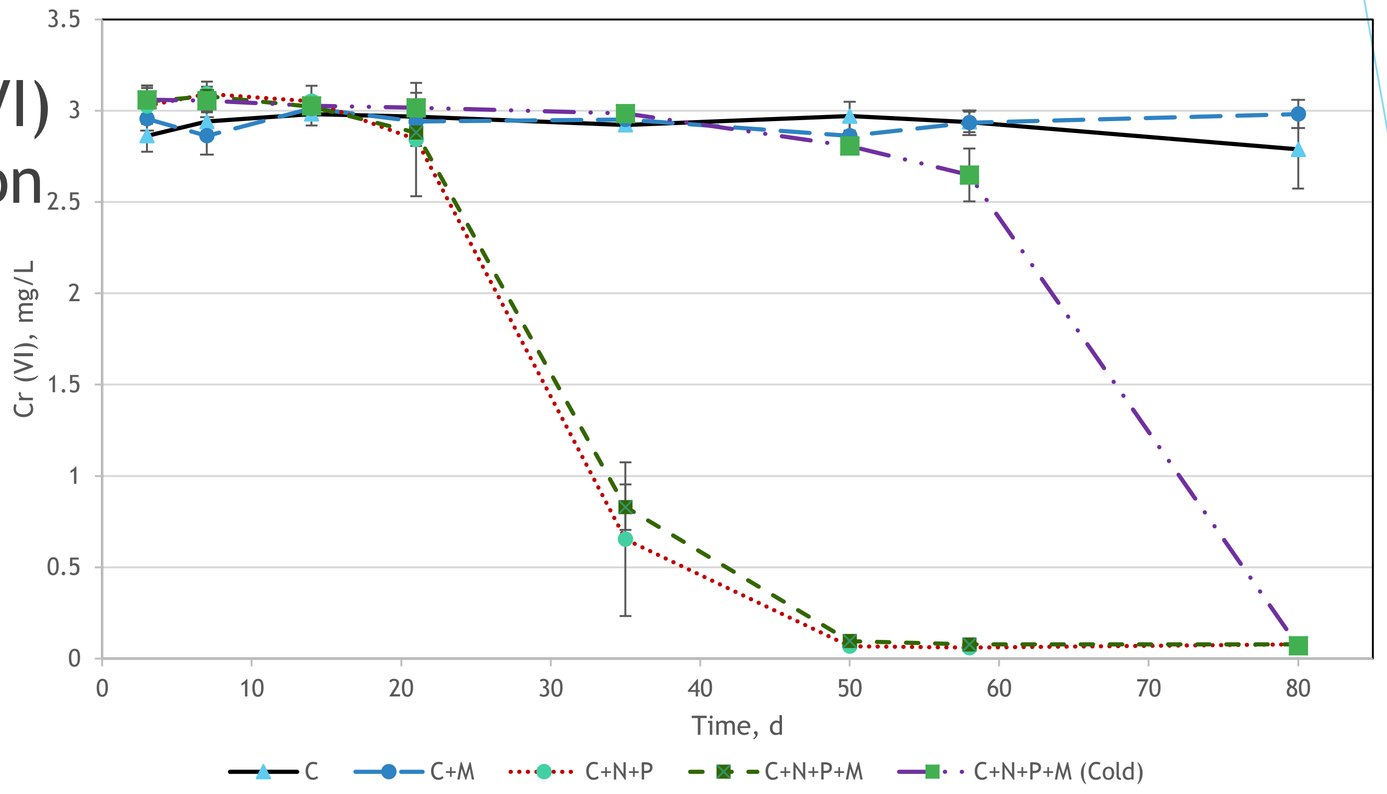
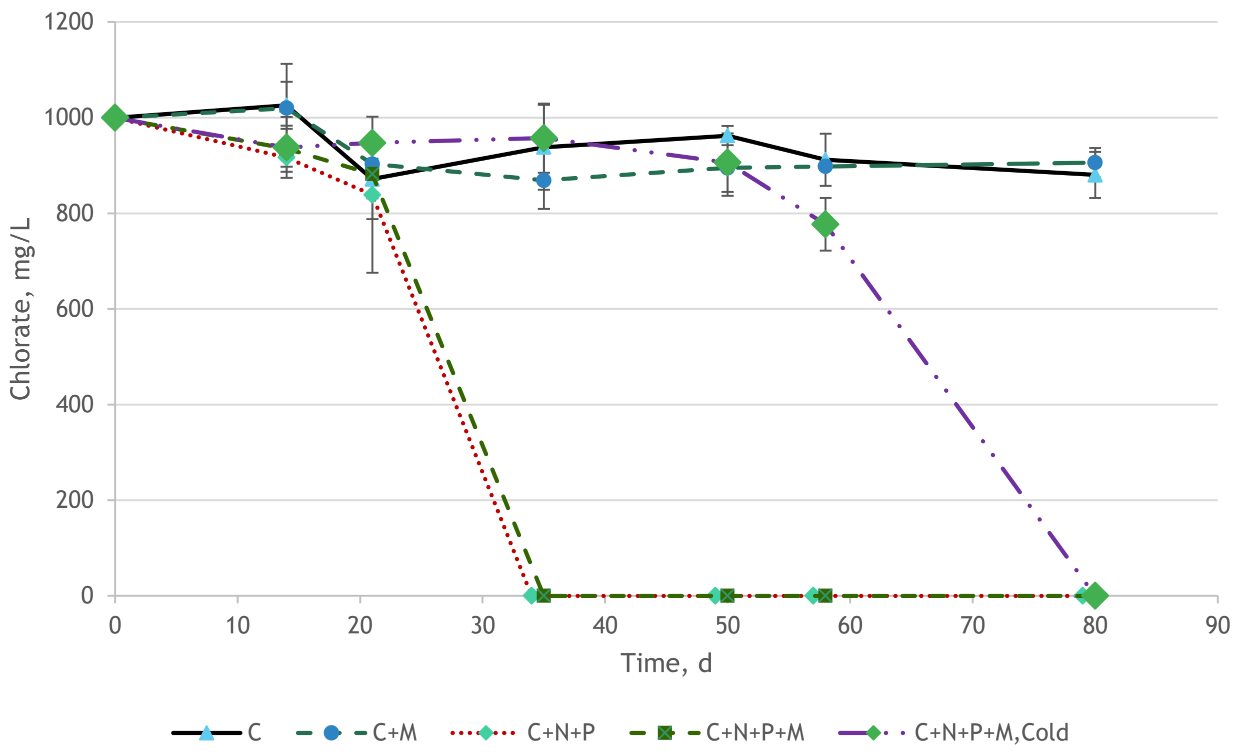
Results

Chromium (VI) Concentration



Results

Chlorate Concentration



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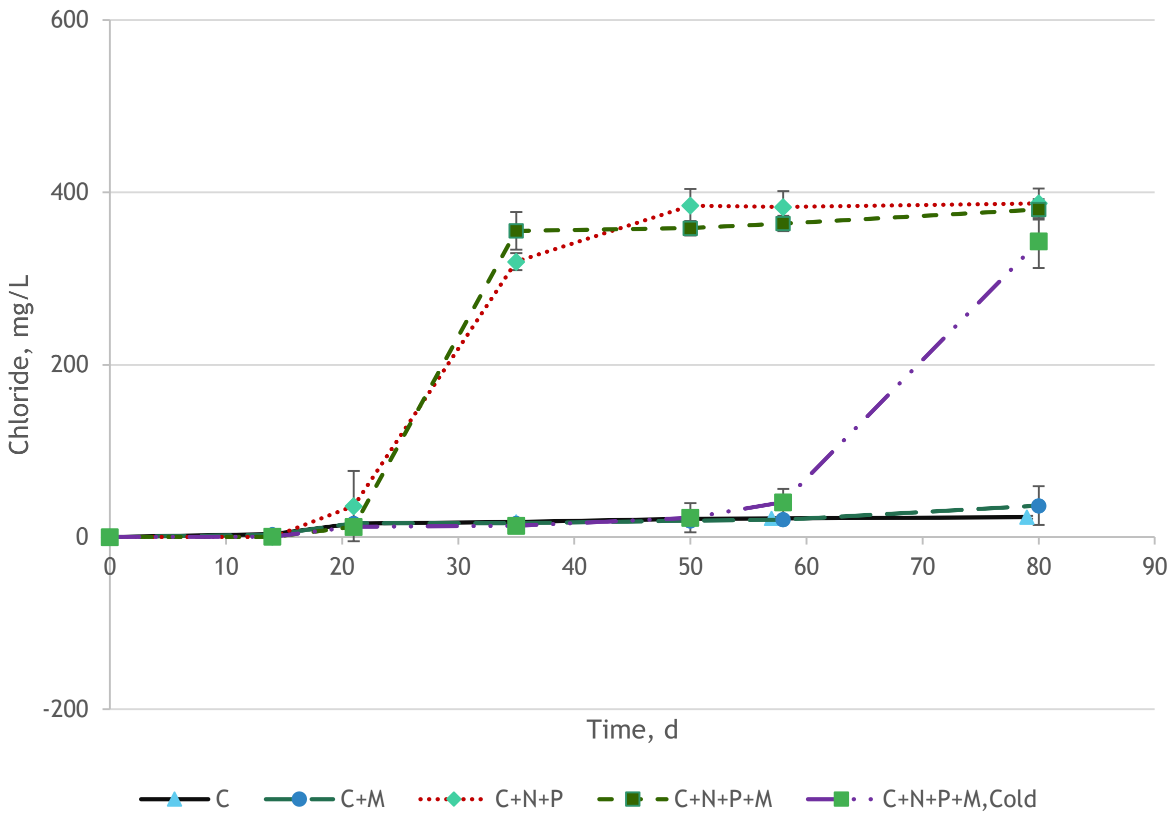
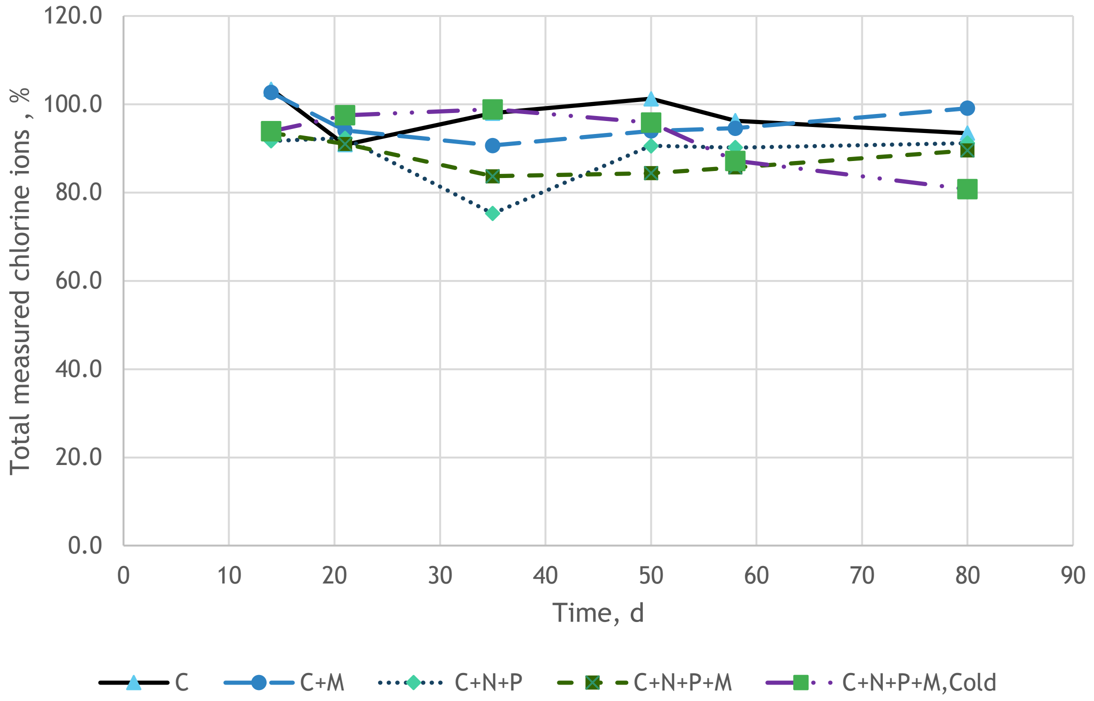
Results

Chloride Concentration



Results

Chlorine ions Concentration



Results

Discussion

- the local microorganisms already present at the site could reduce chlorate and chromate below the applicable drinking water criteria
- Acetate is a proper electron donor for reducing reactions
- Nitrogen and phosphorous are necessary elements to complete the process
- Adding micronutrients as ATCC 1191 media is not effective in the bioremediation
- An in-situ remediation approach of enhanced bioremediation is a suitable option to remediate chlorate and chromate impacted groundwater under cold conditions

Thank you

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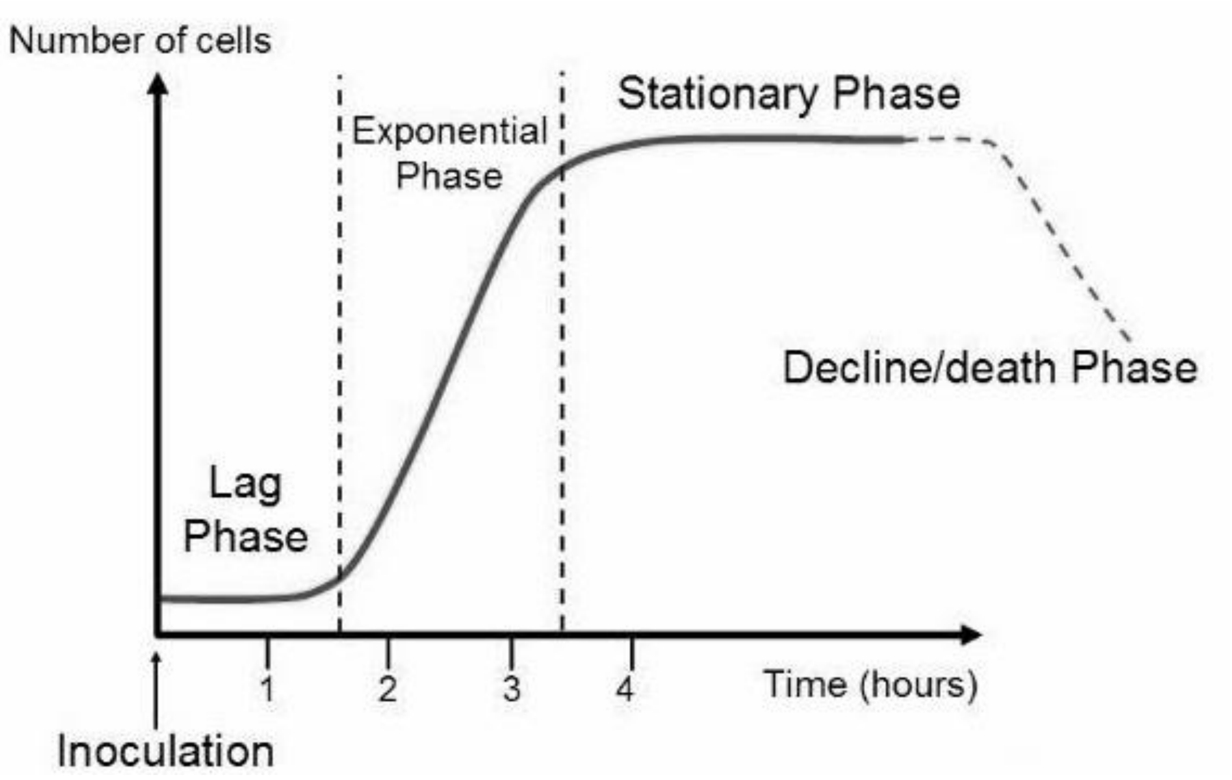
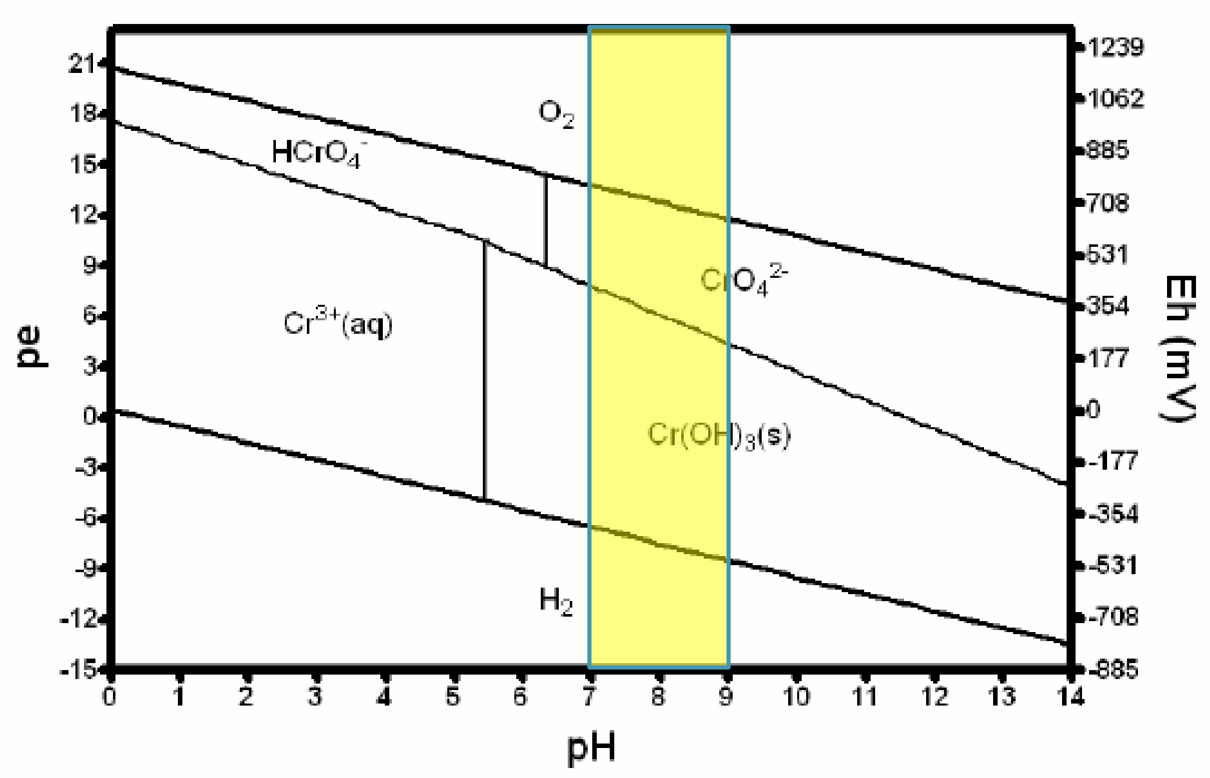
Mineral	add (mg)	conc (g/l) in "1000x sol."	Final conc (g/l) in media
ferric chloride ($FeCl_3$)	1050	2.1	0.0021
cobalt chloride	1000	2	0.002
manganese chloride	500	1	0.001
zinc chloride	500	1	0.001
nickel chloride	500	1	0.001
calcium chloride	250	0.5	0.0005
cupric chloride	250	0.5	0.0005
sodium molybdate	250	0.5	0.0005
nitriloacetic acid	10100	20.2	0.0202



https://orbitbiotech.com/bacterial-growth-curve-generation-time-lag-phase-log-phase-exponential-phase-decline-phase/



Dominic A. Brose, Oxidation-reduction Transformations Of Chromium In Aerobic Soils And The Role Of Electron-shuttling Quinones In Chemical And Microbiological Pathways, 2008, University Of Colorado, Master Thesis