Removal of Cr(VI) by Fe(II) reductive precipitation from groundwaters containing natural organic matter

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Chromate in drinking water

- Worldwide people suffer from groundwater contaminated with chromium
- Sources: Broad application in industry and erosion of natural ophiolitic or ultramafic rocks
- Predominant redox species are Cr(VI) and Cr(III)
- Recent studies reclassified Cr(VI) as toxic, carcinogenic and mutagenic

→ Current discussion about reducing the acceptable limits in drinking water
Chromium removal

- Reduction through Fe(II):
  \[ Cr(\text{VI}) + 3 \text{Fe(II)} \rightarrow Cr(\text{III}) + 3 \text{Fe(III)} \]
  
  \[ [\text{Cr(\text{VI})}]:[\text{Fe(\text{II})}] = 1:3 \]

- Resulting Cr(III) has low solubility:
  Precipitates as Cr(III) hydroxide, adsorbs onto or co-precipitates with iron hydroxides

- Removal of produced solids e.g. by filtration

- Known to be influenced by:
  - pH value
  - Fe(II)/Cr(\text{VI}) ratio
  - Temperature
  - Water composition

→ Fe(\text{II}) reductive precipitation widely used, but so far, role of natural organic matter rarely investigated
Natural organic matter in water

- Commonly found in natural waters and soils
- Wide variety of substances (e.g. lignin, polysaccharides, lipids); Most important humic and fulvic acids

**Influence on chromium removal:**

- Formation of soluble complexes of Fe(III), Cr(III) and humic substances (Buerge, Hug 1998)
- Catalyzing/Accelerating effect on Fe(II) reductive precipitation at pH<6 (Hori et al. 2015)
- Dependent on the type of organic substances

Redox cycling of ferrous and ferric iron in the presence of soil humic acids (SHS) (Wittbrodt, Palmer 1996)
Materials and Methods

- Model groundwater spiked with Cr(VI) and humic acid (Carl Roth)
- Procedure and conditions:
  - Model water
    - Cr(VI), HA
    - Fe(II)
    - Cr(VI): 100 µg/L
    - Humic acid: 0-5 mg/L DOC
    - pH: 6.5 - 8.0
    - FeSO₃ dose: 0.25 - 2.0 mg/L Fe(II)
    - [Cr(VI)]:[Fe(II)] 1:2.3 - 1:18.6
    - 1.8 L
    - 250 rpm 2 min
    - 50 rpm 60 min
    - Filtration 0.45 µm

- Analytics:
  - Cr(VI) photometric with DPC complexation (100mm cuvette)
  - Cr(total) ICP-MS or GFAAS
Influence of pH and Fe(II) dose

- With 1 mg/L Fe(II) total Cr concentrations of 5 µg/L can be achieved over wide pH range when humic acid is absent
- At pH 8 Fe(II) oxidation competition through oxygen

(Gröhlich et al. 2017)
Influence of humic acid on Cr(VI) reduction

- Reduction of Cr(VI) to Cr(III) only influenced by HA at very low Fe(II) dosage (substoichiometric) and at pH 8
- No explicit catalyzing effects on Cr(VI) reduction through humic acid observed

<table>
<thead>
<tr>
<th>pH 7</th>
<th>pH 8</th>
<th>pH 6.5</th>
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<tr>
<td>0</td>
<td>1</td>
<td>3</td>
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<td>2</td>
<td>4</td>
<td>5</td>
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Fe(II) dose [mg/L]:
- 0.25
- 1.0
- 2.0

Detection limit increased due to interferences with humic acid (Gröhlich et al. 2017)

*HA [mg DOC/L]:
- 0
- 2
- 4
- 6
- 8
- 10

*Fe(II) dose [mg/L]:
- 0.25
- 1.0
- 2.0

*Detection limit increased due to interferences with humic acid (Gröhlich et al. 2017)
Influence of humic acid on Cr(III) removal

- Already at DOC of 1 mg/L removal of Cr(III) heavily impaired
- When Cr(VI) fully converted into Cr(III), 30 to 80 µg/L Cr(III) left in solution
- Even with 2 mg/L Fe(II) total Cr values <30 µg/L not achievable

(Gröhlich et al. 2017)
Conclusion

- Cr(VI) is realbly converted into Cr(III) under a wide range of process conditions
- Removal of Cr(III) was observed to be slower and much more prone to be influenced by pH and humic acid
- Without HA Cr(total) values of 5µg/L easily achieved, whereas with HA (1-5 mg/L DOC) 30-80 µg/L Cr(III) remain in solution
- As a likely result of complexation, high amounts of residual Fe (> 0.1 mg/L) were observed

→ Optimization of Cr(III) removal necessary for a versatile application of Fe(II) reductive precipitation
Future Prospects

- Lab-scale pilot experiments including recirculation and submerged microfiltration:
  - Larger contact surface area for Cr(III) adsorption and removal of undesirable and interfering DOC expected
- First experiences:
  - At high sludge concentrations (1 g/L Fe(III)) lower residual concentrations of Cr(VI), Cr(III) and Fe possible
Thanks for you attention

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References


Reaction time

Fe(II) dose [mg/L]:
- 0.25
- 0.5
- 1.0
- 1.5
- 2.0

Cr(VI) and Cr(total) concentrations over time with different Fe(II) doses.
Influence of humic acid and pH

Results and Discussion

Cr(VI) vs. pH:
- pH 8
- pH 7
- pH 6.5

Detection limits:
- Cr(VI) [µg/L]
- HA [mg DOC/L]

Cr(total) concentrations:
- 2 mg/L Fe(II)

pH [-]:
- 8.0
- 7.0
- 6.5

Graph showing the influence of humic acid and pH on Cr(VI) and Cr(total) concentrations.