Effect of Metal-doping of Nanoscale Maghemite on Cr(VI) Adsorption and Nanoparticle Dissolution

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Outline

- Introduction
- Objectives
- Methodology
- Results and Discussions
- Conclusions
Introduction

Hexavalent chromium, Cr(VI):
Highly toxic but valuable
Priority pollutants defined by USEPA
Electroplating, acid mining, refining, petroleum plants
Technologies for heavy metal treatment

- **Chemical precipitation**
  - High equipment costs
  - Large consumption of reagents
  - Large volume of sludge
  - Ineffective recovery of treated metals
  - Potential hazard to environment

- **Ion exchange**
  - High capital and operating cost
  - Fouling
  - Pretreatment

- **Activated carbon adsorption**
  - Large intraparticle diffusion
  - High regeneration cost
  - Low regeneration efficiency
# Magnetic nanoparticle adsorption

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Implications for industrial applications</th>
</tr>
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<tbody>
<tr>
<td>Comparatively large adsorption capacity</td>
<td>Superior removal</td>
</tr>
<tr>
<td>Very short adsorption time</td>
<td>Saved space, especially suitable for crowded cities</td>
</tr>
<tr>
<td>Easy to separate from treated water</td>
<td>Lower capital and operating costs</td>
</tr>
<tr>
<td>Simple to desorb</td>
<td>Easy technical adaptation and maintenance</td>
</tr>
<tr>
<td>No secondary pollution</td>
<td>No potential environmental concern</td>
</tr>
</tbody>
</table>
Maghemite nanoparticles for Cr(VI) removal

Cr(VI) adsorption equilibrium time = 10 min; 50 mg/L of Cr(VI) was reduced to be 0.05 mg/L, below discharge limit.
How to enhance adsorption?

1. Metal-doping technique
   - Increase in surface area or active sites
   - Simple modification method
   - Other parameters not impaired significantly, e.g., adsorption rate, magnetic properties
   - Stable nanoparticles

2. Inorganic coating technique
Objectives

- Promotion of adsorption by metal-doping
- Inhibition of dissolution by metal-doping
- Mechanism studies by Raman spectroscopy
Materials and Methods

❖ **Adsorbent**
   Metal-doped $\gamma$ -Fe$_2$O$_3$ nanoparticle (Me= Al, Mg, Cu, Zn, Ni)

❖ **Adsorbate**
   100 mg/L K$_2$CrO$_4$ + 0.1 M NaNO$_3$

❖ **Batch test**
   Experimental conditions: contact time: 60 min; pH: 2.5;
   shaking rate: 200 rpm; room temperature: 25°C

❖ **Mechanism study**
   Sample for Raman: 5, 50, 100 mg/L Cr(VI) at pH 2.5, 6.5, 8.5
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Analytical methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>ICP</td>
</tr>
<tr>
<td>pH</td>
<td>pH Meter</td>
</tr>
<tr>
<td>Zeta potential</td>
<td>ZETA PLUS</td>
</tr>
<tr>
<td>Particle dimension</td>
<td>TEM</td>
</tr>
<tr>
<td>Particle structure</td>
<td>XRD</td>
</tr>
<tr>
<td>Elemental analysis</td>
<td>XRF</td>
</tr>
<tr>
<td>Complexation</td>
<td>Raman spectroscopy</td>
</tr>
<tr>
<td>Surface area</td>
<td>BET Analyzer</td>
</tr>
<tr>
<td>Magnetism</td>
<td>VSM</td>
</tr>
</tbody>
</table>
Raman spectroscopic studies

- Establish symmetry of surface species
- Distinguish inner-sphere from outer-sphere
  
  (David et al., 1978; Tejedor and Anderson, 1990)

- Raman spectroscopic data about PO$_4^{3-}$, CO$_3^{2-}$, SeO$_4^{2-}$, SO$_4^{2-}$, and AsO$_4^{2-}$ adsorption onto Fe/Al oxides available
  
  (Schulthess and McCarthy, 1990; Su and Suarez, 1998; Wijnja and Cristian, 2000; Goldberg and Johnston, 2001)

- Little detailed information on Raman spectroscopic study of CrO$_4^{2-}$ adsorption onto (modified) iron oxide
Modification of synthesizing methods

- Precipitation method

  Fe$^{2+}$, Fe$^{3+}$, NH$_4$OH
  pH 8.0
  Magnetite particle
  Calcination: 250°C oven
  Maghemite aggregate
  Grinding
  Maghemite nanoparticles
  (> 30 nm, < 80 m$^2$/g)

- Sol-gel method

  Fe$^{2+}$, Fe$^{3+}$, NH$_4$OH (or +Me)
  pH 8.0 (or 10)
  Surfactant
  Magnetite particle
  Oil bath
  Octyl ether
  Maghemite nanogel
  Ethanol washing
  Maghemite nanoparticles
  (< 20 nm, ~ 250 m$^2$/g)
Nanoparticle Synthesis Method (sol-gel)

1.5 M \( \text{NH}_4 \text{OH} \)

\( \text{N}_2 \) gas

\( \text{Al-doped magnetite (Fe}_3\text{O}_4) \)

Thermocouple

250°C oil bath

\( \text{Al-doped maghemite (γ-Fe}_2\text{O}_3) \)
TEM images of Al-doped $\gamma$-Fe$_2$O$_3$

Doping of Al results in preferential crystal growth along [100] direction producing irregular shaped, platy particles, at expense of crystal thickness (Schulze, 1984)
A definite proof of structural incorporation can be produced from a shift in position of XRD peaks, but doping would not change original structure.
Hysteresis loops of Al-doped $\gamma$-$\text{Fe}_2\text{O}_3$

Magnetic properties decreased with increasing Al dosage.
Al-, Cu- and Mg-doping enhanced adsorption capacity; while Cu- and Ni-doping decreased adsorption capacity of previous γ-Fe₂O₃.
## Adsorption and separation

<table>
<thead>
<tr>
<th>Al/(Al+Fe)</th>
<th>Surface area</th>
<th>Adsorption efficiency</th>
<th>Equilibrium time</th>
<th>Magnetic properties</th>
<th>Separation Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>(%)</td>
<td>(m²/g)</td>
<td>(%)</td>
<td>(min)</td>
<td>(emu)</td>
<td>(min)</td>
</tr>
<tr>
<td>0</td>
<td>162</td>
<td>79.8</td>
<td>10</td>
<td>3.48</td>
<td>0.1</td>
</tr>
<tr>
<td>7.5</td>
<td>182</td>
<td>84.3</td>
<td>25</td>
<td>2.26</td>
<td>0.5</td>
</tr>
<tr>
<td>9.3</td>
<td>191</td>
<td>86.7</td>
<td>30</td>
<td>1.78</td>
<td>1</td>
</tr>
<tr>
<td>11.0</td>
<td>198</td>
<td>87.5</td>
<td>60</td>
<td>1.14</td>
<td>5</td>
</tr>
<tr>
<td>13.1</td>
<td>210</td>
<td>88.9</td>
<td>90</td>
<td>/</td>
<td>10</td>
</tr>
</tbody>
</table>
Adsorption mechanism (Raman)

— Cr(VI) adsorption onto Al-doped $\gamma$-Fe$_2$O$_3$

Vibrations for the free CrO$_4^{2-}$ are all Raman active: the nondegenerate $v_1$ at 848 cm$^{-1}$, the doubly degenerate $v_2$ at 342 cm$^{-1}$, the triply degenerate $v_3$ at 882 cm$^{-1}$, and the triply degenerate $v_4$ at 365 cm$^{-1}$
Raman spectra

Effect of pH

100 mg/L Cr(VI) + 5 g/L Al-doped $\gamma$-Fe$_2$O$_3$
at pH 2.5, 6.5, 8.5
Raman spectra
— Effect of surface loading

5, 50, 100 mg/L Cr(VI) + 5 g/L Al-doped γ-Fe₂O₃ at pH 2.5

Counts

Raman shift (cm⁻¹)
## Vibrations between CrO$_4^{2-}$ and Al-doped γ-Fe$_2$O$_3$

| Species               | Cr(VI) (mg/L) | pH  | Frequency (cm$^{-1}$) | $v_1$ | $v_2$ | $v_3$ | $v_4$
|-----------------------|---------------|-----|-----------------------|-------|-------|-------|-------
| K$_2$CrO$_4$ (aq)     |               |     |                       |       |       |       |       
| Al-doped γ-Fe$_2$O$_3$| 5             | 2.5 |                       | 837   | 331   | 867   | 912   | 360   |
| Al-doped γ-Fe$_2$O$_3$| 50            | 2.5 |                       | 835   | 331   | 868   | 894   | 366   |
| Al-doped γ-Fe$_2$O$_3$| 100           | 2.5 |                       | 831   | 338   | 858   | 876   | 926   | 359   | 369   |
| Al-doped γ-Fe$_2$O$_3$| 100           | 6.5 |                       | 840   | 341   | 863   | 932   |       | 365   |
| Al-doped γ-Fe$_2$O$_3$| 100           | 8.5 |                       | 848   | 339   |       |       |       | 354   |
Inner-sphere complex between Cr(VI) and Al-doped γ-Fe$_2$O$_3$

Monodentate

Bidentate mononuclear*

Bidentate binuclear*

(* Together with data from Hiemstra et al., 1989; McBride, 1994; Fendorf et al., 1997; Wijnja and Schuthess, 2000)
Adsorption isotherms

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$q_m$ (mg/g)</th>
<th>$b$ (L/mg)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-doped $\gamma$-Fe$_2$O$_3$</td>
<td>22.68</td>
<td>0.138</td>
<td>0.993</td>
</tr>
<tr>
<td>Pure $\gamma$-Fe$_2$O$_3$</td>
<td>19.42</td>
<td>0.319</td>
<td>0.997</td>
</tr>
</tbody>
</table>
## Comparison of adsorbents

<table>
<thead>
<tr>
<th>Type of adsorbents</th>
<th>$q_m$ (mg/g)</th>
<th>Equilibrium time (h)</th>
<th>Optimum pH</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut tree sawdust</td>
<td>3.46</td>
<td>3</td>
<td>3.0</td>
<td>(Selvi et al., 2001)</td>
</tr>
<tr>
<td>Lignin</td>
<td>5.64</td>
<td>24</td>
<td>2.5</td>
<td>(Lalvani et al., 2000)</td>
</tr>
<tr>
<td>Distillery sludge</td>
<td>5.7</td>
<td>1.75</td>
<td>3.0</td>
<td>(Selvaraj et al., 2003)</td>
</tr>
<tr>
<td>Blast-furnace slag</td>
<td>7.5</td>
<td>6</td>
<td>1.0</td>
<td>(Srivastava et al., 1997)</td>
</tr>
<tr>
<td>Diatomite</td>
<td>11.55</td>
<td>2</td>
<td>3.0</td>
<td>(Dantas et al., 2001)</td>
</tr>
<tr>
<td>Aluminum oxide</td>
<td>11.7</td>
<td>8</td>
<td>4.0</td>
<td>(Gupta et al., 1999)</td>
</tr>
<tr>
<td>Anatase</td>
<td>14.56</td>
<td>24</td>
<td>2.5</td>
<td>(Weng et al, 1997)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>15.47</td>
<td>3</td>
<td>4.0</td>
<td>(Sandhya and Tonni, 2004)</td>
</tr>
<tr>
<td>Beech sawdust</td>
<td>16.13</td>
<td>1.33</td>
<td>1.0</td>
<td>(Acar and Malkoc, 2004)</td>
</tr>
<tr>
<td>Hazelnut shell</td>
<td>17.7</td>
<td>5</td>
<td>2.0</td>
<td>(Cimino et al., 2000)</td>
</tr>
<tr>
<td>Spent grain</td>
<td>18.94</td>
<td>8</td>
<td>2.0</td>
<td>(Low et al., 2001)</td>
</tr>
<tr>
<td><strong>Al-doped γ-Fe$_2$O$_3$</strong></td>
<td><strong>22.68</strong></td>
<td><strong>0.5</strong></td>
<td><strong>2.5</strong></td>
<td><strong>Present study</strong></td>
</tr>
<tr>
<td>Larch bark</td>
<td>31.25</td>
<td>48</td>
<td>3.0</td>
<td>(Aoyama and Tsuda, 2001)</td>
</tr>
</tbody>
</table>

**Note:** Cr(VI) Adsorption capacity and equilibrium time at room temperature of 22.5 ± 2.5°C
1) Al-O bond energy (513 kJ mol\(^{-1}\)) > Fe-O bond energy (390 kJ mol\(^{-1}\)),

2) More energy to remove simultaneously two center atoms due to effect of binuclear complexes (Cornell et al., 2003)
Conclusions

- Optimal Al dosage is 9.3 mol%
- Enhanced adsorption capacity from 19.4 mg/g to 22.7 mg/g by Al-doping
- *Insignificant* nanoparticle dissolution under experimental condition; Al-doping inhibited dissolution by 30%
- Complexation changed from outer-sphere into *inner-sphere complexation* by Al-doping
Thank you