Nanostructurated systems for water remediation process

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Motivation: Environmental Pollutants

Water resources

- 0.3% sweet water available in rivers, damps, and lakes.
- Several sources of contamination (natural and anthropogenic).

![Water resources diagram]

Risk of Arsenic Contamination

![Risk of Arsenic Contamination map]

Source: Schwarzenbach et al., 2010. United Nations Environment Programme (UNEP)

- Inorganic Arsenic pollutes the groundwater, occurs naturally on earth in small accounts.
- Inorganic Arsenic is a well known carcinogen (skin, lung, prostate).
Center for the development of Nanoscience & Nanotechnology

Investigation areas:
- Simulations
- Magnetic Nanostructures
- Chemistry of Nanostructures
- Chemical Physics
- Packaging Technology
- Nanobiomedicine

Magnetic nanoparticles
Iron nanoparticles for the removal of Arsenic

**Synthesis:** Chemical reduction \((\text{FeCl}_3 \cdot 6\text{H}_2\text{O} \text{ with } \text{NaBH}_4)\) [1]

Iron oxide nanoparticles (D ~ 50-100 nm) are synthesized as magnetite, hematite and other iron oxides.

HRTEM of nZVI(a) before and (b-d) after arsenic sorption.

Elemental mapping after arsenic sorption.

- Elemental mapping shows presence of aggregate nanoparticles
- Homogeneous distribution of As, Fe and O on the surface.


Next step: Combining elements
Arsenic sorption on FeCu nanoparticles

FeCu (BMNPs) synthesis: simultaneous chemical reduction [1]
- **Two concentrations**: Fe\textsubscript{0.9}Cu\textsubscript{0.1} and Fe\textsubscript{0.5}Cu\textsubscript{0.5}
- Precursors: FeCl\textsubscript{3}·6H\textsubscript{2}O, CuCl\textsubscript{2}·2H\textsubscript{2}O
- Reduction agent: NaBH\textsubscript{4}

XRD of (a) nZVI, (b) Fe\textsubscript{0.9}Cu\textsubscript{0.1}, (c) Fe\textsubscript{0.5}Cu\textsubscript{0.5}, and (d) Cu NPs. Symbols: (●) = Fe\textsuperscript{0}, (▲) = Cu\textsuperscript{0}, (■) = cuprite, (▼) = tenorite, and (◀) = magnetite.

Fe\textsubscript{0.9}Cu\textsubscript{0.1} shows the highest removal
Capacity: Why?

Nanoparticle systems

Size, shape and composition of nanoparticles affect their physico-chemical properties.
Novel structures can be used in innovative improved applications.

Relying on physical experiments to explore numerous configurations determining possible candidates is a major challenge.

Modeling nanoparticles and simulations offers a possibility to find and study stable configurations.

Possible solution: MD with LAMMPS
We need to find stable nanoparticle morphologies at nanoscale.

**Modeling Nanoparticles**

**LAMMPS setup**
- Molecular dynamics simulation using EAM potential for FeCu systems [1]
- MD annealing process. NVT ensemble at each cycle
- Time step: 1 fs
- Cycle steps: $3 \cdot 10^6$
- Temperature: 900K

**Local minima searching**
- MD annealing allows a restricted exploration of energy landscape to find good candidates in a local region.

Bimetallic nanoparticles
Fe-Cu

Structural optimization based on cycles of thermal annealing and minimizations.

Morphology of stable FeCu nanoparticles Depends on the concentration and size.

Core-Shell and Janus-like structures obtained at low and high Cu concentrations respectively.

Continuous model adjusted for immiscible elements.

Bimetallic nanoparticles
Fe-Cu

How do we use this information in the experiment?

Controlled synthesis of magnetic nanoparticles.

Linear mapping of FeCu BMNPs. The concentration profiles of the Fe$_{0.9}$Cu$_{0.1}$ and Fe$_{0.5}$Cu$_{0.5}$ samples.

Linear Atomic distribution of Fe and Cu in simulated FeCu BMNPs. Yellow lines show the calculated linear mapping of each particle at Fe$_{0.9}$Cu$_{0.1}$ and Fe$_{0.5}$Cu$_{0.5}$ respectively.

What is happening at the atomic level?
Theoretical study of arsenic sorption
We consider two oxidation states: As(III) and As(V) and subspecies.

Subspecies are controlled by acidic conditions present in water.

Electronic configuration and charge density allow to identify reactive sites of As species.

**VASP setup**
- Structural Optimization of surface and molecules.
- GGA+U method with PAW.
- Exchange-correlation functional PBE
- $E_{\text{cut}} = 400 \text{eV}$

Relaxation of Fe3O4(001) leads to a $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction.
Fe$_3$O$_4$(001) + As species

**Adsorption energies**

<table>
<thead>
<tr>
<th>Energy</th>
<th>$\Delta E$(eV)</th>
<th>O$_2$</th>
<th>AsO(OH)$_2$</th>
<th>AsO(OH)$_3$</th>
<th>AsO$_4$(OH)$_2$</th>
<th>AsO$_4$(OH)$_2$</th>
<th>AsO$_3$(OH)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$(kJ/mol)</td>
<td>107.679</td>
<td>199.438</td>
<td>280.442</td>
<td>445.769</td>
<td>231.955</td>
<td>321.619</td>
<td>293.899</td>
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<table>
<thead>
<tr>
<th>As(III)</th>
<th>As(V)</th>
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<tr>
<td>$O_2$</td>
<td>AsO(OH)$_2$</td>
</tr>
<tr>
<td>1.116</td>
<td>2.067</td>
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</tbody>
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Fe₃O₄(001) / As(III)

- Adsorption energy:

\[ E_{ads} = E_{Surf} + E_{Mol} - E_{Total} \]

- \( E_{ads} = 2.07 \) eV.

<table>
<thead>
<tr>
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<th>d (angs)</th>
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<tbody>
<tr>
<td>d(O – Fe)</td>
<td>2.21</td>
</tr>
<tr>
<td>d(As – O)</td>
<td>1.9</td>
</tr>
<tr>
<td>d(As - Fe)</td>
<td>3.54</td>
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</tbody>
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Fe$_3$O$_4$(001)/ As(V)

- Adsorption energy: 2.4 eV.

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<tbody>
<tr>
<td>d(O – Fe)</td>
<td>2.09</td>
</tr>
<tr>
<td>d(As – O)</td>
<td>1.71</td>
</tr>
<tr>
<td>d(As - Fe)</td>
<td>3.2</td>
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Bandstructure of Fe$_3$O$_4$(001) H$_2$AsO$_4$
Conclusions and perspectives

- FeCu particles obtained by chemical reduction are suitable for removal of water contaminants. Morphology and concentration are crucial in the removal process.

- Molecular dynamics simulations on bimetallic particles show the size and concentration effects on the morphology of bimetallic nanoparticles.

- The optimal condition of nanoparticles for water remediation is the bimetallic Core-Shell structure.

- DFT calculations show bond formation between iron oxide surfaces and As(III) and As(V) complexes, where As(V) presents the higher adsorption energy.

- Future Work: Competition between pollutants (As, Pb, Al)
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