COMPARATIVE STUDY OF ARSENIC REMOVAL EFFICIENCY FROM WATER BY ADSORPTION AND PHOTOCATALYTIC OXIDATION WITH TITANIUM DIOXIDE

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Background

- The significantly high contamination level of arsenic has been reported for many countries as India, USA, Mexico, China, Argentina and Turkey.
- Arsenic is severely harmful to the human health and long term exposure to arsenic can lead to cancer of the lungs, skin, kidney and liver.
- World Health Organization (WHO) lowered arsenic level in drinking water from 50 to 10 ppb on Jan 23, 2006.

Arsenic is naturally occurring element.

### Natural sources:
- Dissolution and weathering of rocks
- Volcanoes
- Forest fires

### Manmade/man-affected sources:
- Agriculture
- Mining and industrial wastes

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Chemistry Behind Arsenic

- In natural water, arsenic occurs both in organic and inorganic forms.
- Inorganic arsenic exists in -3, 0, +3 and +5 oxidation states in aquatic systems. The elemental state 0 and -3 are quite rare as compared to +3 and +5 oxidation states.

\[
\begin{align*}
\text{As (III)} & \text{ - As}^{+3} \text{ Arsenite} \\
\text{As (V)} & \text{ - As}^{+5} \text{ Arsenate}
\end{align*}
\]

- As (III) has greater toxicity and mobility than As (V).
- Organic arsenic is detoxified by methylation process.

Inorganic arsenic is needed a well-established treatment.
Arsenic Treatment Options

- Coagulation – coprecipitation
- Ion exchange technique
- Membrane technologies
- Reverse osmosis
- Nanofiltration
- Bioremediation
- Adsorption
Objectives

- Synthesis of anatase nanoparticles for adsorption and photocatalytic oxidation processes

- Analysis of the arsenic adsorption on the surface of anatase nanoparticles since relatively few studies exist on that field

- Understanding the photocatalytic oxidation mechanism of As(III) by using anatase nanoparticles under UV illumination
Adsorbent Material- Titanium Dioxide

- It is widely used as a pigment for paints, plastics, cosmetics and toothpastes due to the its brilliant whiteness.

- It possesses a high potential for the environmental application due to the its physical and chemical stability, lower cost, nontoxicity and resistance to corrosion.

- It can be classified as three types (anatase, rutile and brookite) in terms of its crystal structure.

- Anatase has higher photocatalytic properties than rutile.

- In this study, anatase mineral type was used as an adsorbent material.

A sol-gel method was used to synthesize the anatase nanoparticles. This method was selected because it creates amorphous particles, allowing us to control the crystallinity.

<table>
<thead>
<tr>
<th>Precursor Solution</th>
<th>Hydrolysis Solution</th>
<th>Final Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTIP (ml)</td>
<td>2-propanol (ml)</td>
<td>Distilled water (ml)</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>2,5</td>
</tr>
</tbody>
</table>

The gel preparation process was started when the precursor and hydrolysis solutions were mixed together under continuous stirring at room temperature.

After certain period of mixing, sample was filtrated and annealed at different temperatures for 2 h.
SEM Images

Mag = 90.00 K X

EHT = 2.00 kV
VP Target = 15 Pa
WD = 8 mm
Detector = SE2

Date: 117 Feb 2010
Aperture Size = 30.00 μm
XRD Results

Anatase U350 UC

Intensity

Anatase U450 UC

Intensity

Anatase 450°C

Intensity

Anatase 350°C

Intensity

A(101)

Intensity

Anatase - commercial

Intensity
Batch Adsorption Experiments

Procedure:

1. Prepare working solution - (contains arsenic species)
2. Add adsorbent material
3. Arrange pH with acid or base
4. Filtrate solution with 0.45µm syringe

Analysis of solutions with ICP-OES

Adsorption efficiency depends on optimum:
- pH
- Contact time
- Experiment temperature
- Adsorbent amount
- Initial arsenic concentration
Effect of Contact Time

Arsenic uptake ($q_e$) increases with increasing contact time until the state of equilibrium is reached due to saturation of adsorbent’s active sites.

Over 81% of the arsenate is taken up within 60 min exposure and maximum 94.7% arsenate have been removed within 2 hours reaction time by anatase nanoparticles.

The maximum 56% of arsenite have been taken up within 36 h.

$$q_e = \frac{C_0 - C_e}{X}$$
## Sorption Kinetics

### Kinetic Models

<table>
<thead>
<tr>
<th>Kinetic Models</th>
<th>Parameters</th>
<th>As(III)</th>
<th>As(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pseudo-first order:</strong></td>
<td>$k_1$ (h$^{-1}$)</td>
<td>0.032</td>
<td>0.024</td>
</tr>
<tr>
<td>$\log(q_e - q_t) = \log q_e - k_1 t$</td>
<td>$q_e$ (mg/g)</td>
<td>0.338</td>
<td>0.283</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.941</td>
<td>0.470</td>
</tr>
<tr>
<td><strong>Pseudo-second order:</strong></td>
<td>$k_2$ (g/mg h)</td>
<td>6.711</td>
<td>18.08</td>
</tr>
<tr>
<td>$t = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$</td>
<td>$q_e$ (mg/g)</td>
<td>0.152</td>
<td>0.239</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td><strong>0.997</strong></td>
<td><strong>0.999</strong></td>
</tr>
<tr>
<td><strong>Interparticle diffusion:</strong></td>
<td>$k_p$ (mg/g h$^{1/2}$)</td>
<td>0.016</td>
<td>0.019</td>
</tr>
<tr>
<td>$q_t = k_p t^{1/2} + C$</td>
<td>$C$ (mg/g)</td>
<td>0.063</td>
<td>0.151</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.810</td>
<td>0.483</td>
</tr>
</tbody>
</table>
Effect of pH

Initial arsenic concentration = 5 mg/L  adsorbent amount = 5 g/L, contact time = 24 h

Effect of Adsorbent Amount
Adsorption Isotherms

**Comparaison of As(III) adsorption potential of anatase nanoparticles with other adsorbents**

<table>
<thead>
<tr>
<th>Name of Adsorbent</th>
<th>Adsorption capacity (mg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron oxide sand</td>
<td>0.029</td>
</tr>
<tr>
<td>Activated alumina</td>
<td>0.1803</td>
</tr>
<tr>
<td>Red mud</td>
<td>0.66</td>
</tr>
<tr>
<td>Iron oxide impregnated activated alumina</td>
<td>0.734</td>
</tr>
</tbody>
</table>

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}} b} + \frac{C_e}{q_{\text{max}}} \\

\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]

\[
q_e = q_{\text{max}} \left(1 - \frac{C_e}{C_{\text{max}}} \right) \quad \text{Langmuir}
\]

<table>
<thead>
<tr>
<th>Anatase nanoparticles</th>
<th>( R^2 )</th>
<th>( q_{\text{max}} ) (mg/g)</th>
<th>( b ) (1/mg)</th>
<th>( R^2 )</th>
<th>( K_f )</th>
<th>( n_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III)</td>
<td>0.998</td>
<td>0.403</td>
<td>5.503</td>
<td>0.801</td>
<td>0.231</td>
<td>2.898</td>
</tr>
<tr>
<td>As(V)</td>
<td>0.982</td>
<td>1.145</td>
<td>3.460</td>
<td>0.960</td>
<td>2.081</td>
<td>0.707</td>
</tr>
</tbody>
</table>

The calculated free energy values are -13.48 kJ/mol for As(III) and As(V) at 298 K.

The negative free energy values indicate the feasibility of the process and the spontaneous nature of adsorption.
Photocatalytic Oxidation of Arsenite

• Anatase is the widely used photocatalyst due to its strong oxidizing power and favorable band gap energy.

• Photocatalysis can rapidly oxidize arsenite (As(III)) to less toxic arsenate (As(V)) by using following mechanism*:

⇒ Generation charge carriers and photooxidants

\[
\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2(e_{cb}^- + h_{vb}^+) \quad (1)
\]
\[
e_{cb}^- + O_2 \rightarrow O_2^- \quad (2)
\]
\[
h_{vb}^+ + OH^- \rightarrow HO^- \quad (3)
\]

⇒ Arsenic(III) oxidation

\[
\text{As(III)} + \text{HO}^- \rightarrow \text{As(IV)} + \text{OH}^- \quad (4)
\]
\[
\text{As(III)} + O_2^- \rightarrow 2H^+ \rightarrow \text{As(IV)} + \text{H}_2\text{O}_2 \quad (5)
\]
\[
\text{As(IV)} + O_2 \rightarrow \text{As(V)} + O_2^- \quad (6)
\]

Photocatalytic Oxidation Experiments

As(III) Stock solution

Adding anatase nanoparticles to the solution

0.45 µm filtration

Molybdenum Blue Method

Analysis of reduced and unreduced samples with UV spectrophotometer

Analysis of Total Arsenic

UV-A/TiO₂ illumination

Analysis of Total Arsenic

Arsenic (V) forms complex with molybdenum

Analysis of Total Arsenic

Analysis of Total Arsenic
The effect of illumination time on arsenite oxidation was examined at an initial arsenite concentration of 5 mg/l and adsorbent amount 5 g/l at pH 4.

Arsenite species could be totally oxidized to arsenate only by UV-light illumination, but the reaction rate was slower than the TiO$_2$ photocatalyzed reaction.
Effect of Adsorbent Amount on Total Arsenic Removal

- Experimental conditions:
  - Illumination time = 3.5 h, contact time = 4 h.
  - Without illumination, contact time = 24 h.

- Arsenic removal efficiency is greatly affected by adsorbent dosage.
- The optimum application amount of anatase nanoparticles is around 3-5 g/l for the photocatalytic experiment.
Effect of Contact Time

- Experimental conditions:
  - anatase nanoparticles dosage = 5 g/L, pH = 4, initial arsenic concentration = 5 mg/L.

- The adsorption increased linearly from the beginning and rapidly reached a plateau value within 4 h for UV-illuminated anatase nanoparticles.
Conclusion

- By using sol-gel method, anatase nanoparticles crystal was synthesized with particle size between 40-100 nm.
- Adsorption experiments were performed for anatase nanoparticles to obtain optimum pH, contact time and adsorbent amount.
- The low adsorption capacity of anatase nanoparticles from aqueous solution usually limit its application in contaminated water treatment.
- Using photocatalytic oxidation, arsenite can rapidly oxidized to arsenate, which is less toxic and mobile in aquatic environment.
- The removal capacity of As(III) from water was improved by UV- irradiation about ~90 % as compared with adsorption process of anatase nanoparticles.
Thank you for your attention..

Any Questions?
Calculation of $q_e$

- The amount of arsenic adsorbed per unit weight of the adsorbent was calculated by using the following equation:

\[ q_e = \frac{C_o - C_e}{X} \]

$q_e$: is the concentration of the arsenic on the adsorbent (mg/g), $C_o$ and $C_e$: are the initial and the equilibrium concentrations of the arsenite or arsenate in the solution (mg/L), $X$: is the dosage of the adsorbent material used (g/L).