Physicochemical Denitrification Process for Drinking Water Resources at Ambient Conditions

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Nitrogen oxide decomposition to N\textsubscript{2} is economically rational

This is absolutely different from CO\textsubscript{2} decomposition which was proposed in the past.

Benefits of nitrogen oxides decomposition technology:

- N\textsubscript{2}O decomposition contributes to mitigation of global warming.
- NO decomposition contributes to removal of air pollutant.
- NO\textsubscript{3}\textsuperscript{-}, NO\textsubscript{2}\textsuperscript{-} decomposition contributes to groundwater purification.
Conventional nitrogen oxides decomposition processes are not sustainable. Why?

Conventionally this energy was supplied through H₂, noble-metal catalyst or others, resulting in energy-intensive processes.

Degree of oxidation

E

N₂, O₂, C

N₂O, C₂O?

NO, CO

NO₂, CO₂

+ H₂O

NO₃⁻, CO₃²⁻
Catalytic processes proposed for nitrogen oxide decomposition are “three-body collision”.

- These are an energy-intensive process requiring lots of high quality energy, e.g., H₂, NH₃ or hydrocarbon.
- Head-on collision of NOₓ and H₂ is not sufficient to react at ambient conditions.
- Biological process proceeds at more mild conditions, but too sluggish.
RITE PJ: Catalytic decomposition of \( \text{NO}_3^- \) in flow of \( \text{H}_2 \)

Results:
Large amount of byproducts: \( \text{NO}_2^- \) and \( \text{NH}_3 \)


Similar unsustainable results have been reported by Hokkaido University and others.
Dr. T. Okuhara (Hokkaido Univ)

40% remained

Cu-Pd cluster AC
Pd/β-zeolite

Byproduct NH₃ is formed.

Our greener & sustainable idea: spillover-based NO x decomposition

- NO x decomposition is possible at ambient temperature and pressure.
- Energy input to dissociate NO x is minimal.
Requisite materials for this greener & sustainable process

Properties of materials:
1. charge-transferable surface
2. serve sufficiently reactive sites even in aqueous conditions.
3. chemically insoluble
4. economical
5. available worldwide
6. non-toxic (for food-level safety, heavy metal free)
Conventional adsorption process

Cost-effective NOx decomposition process has not been known using conventional adsorption process and well-known materials such as activated carbon and ion exchange resin.

Effluent is not free from NO$_2^-$ or NO$_3^-$. 
Our simple device to generate metabolites-free water with minimal energy at ambient conditions: conceptual drawing

Charged surface is generated on materials at low voltage.

Voltage ( <5V ) & ”zero” current ( <1mA )

Water free from metabolites (NO$_2^-$, NO$_3^-$) and pollutants (F$^-$, P, As)

Notes: No use of organics, bacteria, NH$_3$, or H$_2$ as reductant of NO$_x^-$.
Postulated Mechanism for Decomposition of N and S Oxides

Feed containing $\text{H}^+$, $\text{NO}_3^-$, $\text{NO}_2^-$, and $\text{SO}_4^{2-}$

N$_2$(↑) , S (fixed on materials)

Process at anode: dissociation of water and charge transfer

$\text{H}_2\text{O} \Rightarrow \text{H}^+ + \text{OH}^- \Rightarrow \text{H}_2\text{O}$

- $\text{H}^+ + \text{NO}_3^-, \text{NO}_2^- \text{ or } \text{SO}_4^{2-} \Rightarrow \text{N}_2 \text{ or } \text{S} + \text{H}_2\text{O} + \text{e}^- \quad$ (decomposition of oxoanions)
- $\text{OH}^- + \text{H}^+ \Rightarrow \text{H}_2\text{O}$ \quad (neutralization of acidic water)
# Treatment of goldfish bath water

<table>
<thead>
<tr>
<th>Ions</th>
<th>Feed (ppm)</th>
<th>Feed 1.1L (ppm)</th>
<th>Feed 1.76L (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{PO}_4^{3-}$</td>
<td>2.95</td>
<td>&lt;0.01</td>
<td>2.39</td>
</tr>
<tr>
<td>$\text{Cl}^-$</td>
<td>23.5</td>
<td>97.0</td>
<td>48.5</td>
</tr>
<tr>
<td>$\text{NO}_3^-$</td>
<td>143</td>
<td>0.66</td>
<td>0.67</td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}$</td>
<td>68.5</td>
<td>5.44</td>
<td>111</td>
</tr>
<tr>
<td>pH</td>
<td>3.84</td>
<td>6.90</td>
<td>6.77</td>
</tr>
</tbody>
</table>

Volume of reactor = 0.1L
Total volume of feed = 1.76 L
Feeding time = 4 h
$SV = \frac{1.76 \text{ L}}{4 \text{ h}} / 0.1 \text{ L} = 4.4$
Materials balance of water treatment

<table>
<thead>
<tr>
<th>Constituent</th>
<th>uptaken (mequiv.)</th>
<th>released (mequiv.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_4^{2-}$</td>
<td>1.11</td>
<td>-</td>
</tr>
<tr>
<td>HPO$_4^{2-}$</td>
<td>0.12</td>
<td>-</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>4.04</td>
<td>-</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>-</td>
<td>2.71</td>
</tr>
<tr>
<td>Heavy metals</td>
<td>&lt; 0.05</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Total</td>
<td>5.27</td>
<td>2.71</td>
</tr>
</tbody>
</table>

Totally different ⇒ not simple ion exchange

(Other anions (CO$_3^{2-}$, OH$^-$, H$^+$) may be involved in this treatment process. Open for study)
FTIR spectrum of material used at anode

Oxygen of $\text{NO}_3^-$, $\text{SO}_4^{2-}$ were transferred?

- Wave number, cm$^{-1}$
  - 1157 cm$^{-1}$
  - 1217 cm$^{-1}$
  - 1518 cm$^{-1}$
  - 1560 cm$^{-1}$ (CO$_3^{2-}$)
  - 2360 cm$^{-1}$
  - 2333 cm$^{-1}$ (CO$_2$ gas)

Almost no water
Speciation of sulfur in activated carbon by wave-dispersed PIXE

Sulfate was reduced to elemental sulfur.
Conclusion (a)
Operational features

1. Contact time of water with material is very short ( <10min ).

2. Decomposition of nitrate/nitrite and sulfate is feasible without side reactions to form NH$_3$.

3. It works at room temperature and at normal pressure.

4. Driving energy is minimal.
Conclusion (b)
Requisite materials in this process

This innovative process does not require:

1. bacteria
2. organic fertilizer or chemicals
3. hydrogen gas
or
4. expensive noble metal-loaded catalysts
Conclusion (c)
Quality of treated water

1. Treatment lowers concentration of NO$_3^-$ from 140ppm to 0.7ppm.


3. NH$_3$ will be never admixed into treated water.

4. Device possesses large neutralization capacity. Acidic groundwater of pH 4 can be neutralized to 7.

5. All the treated water can be utilized. Only 30-40% for conventional reverse osmosis separation method