Green Chemistry Advances at EPA

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Sustainable development is an evolving process that improves the economy, the environment, and society for the benefit of current and future generations.

- President’s Council on Sustainable Development 1998
What is Green Chemistry?

- Use of latest technologies?
- Good development chemistry?
Green Chemistry Definition

Green Chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products.
Twelve Principles of Green Chemistry

1. It is better to prevent waste than to treat or clean up waste after it is formed.

2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. Synthetic processes should avoid use and generation of toxic and environmentally damaging substances.

4. Chemical products should be as effective as possible but with minimum toxicity.

5. Auxiliary substances, such as solvents and separation agents should be avoided or should be as innocuous as possible.

6. Energy requirements should be low; extreme temperatures and pressures should be avoided.
Twelve Principles of Green Chemistry

7. Raw materials should be from renewable sources
8. Derivatization for blocking group protection and property modification should be avoided
9. Catalytic reagents should be used when possible because of their specificity and minimum amounts required
10. Chemical products should be designed so that at the end of their lifetime they readily break down to harmless products
11. The best analytical and monitoring capabilities should be employed to allow real-time, in-process monitoring that prevents formation of hazardous substances
12. Substances and forms of them used should be chosen to avoid potentially harmful releases, fires, and explosions
Green Chemistry Goals

• Ensure principles of green chemistry are widely used

• Decrease adverse impacts to human health and the environment via improved design of products and processes

• Promote innovation and economic development

• Improve competitiveness of US goods on global market
Green Chemistry and Engineering

The adoption of the green chemistry and engineering requires a paradigm shift to occur.

Decaffeination via CH$_2$Cl$_2$  Decaffeination via CO$_2$  Coffee Beans with no caffeine
EPA Research Approach

• Lead by example: Internal research effort
• Chemical Safety for Sustainability
  – Inherent properties
  – life-cycle considerations
• Research collaborations
  – Industrial/interagency/academic
• Commercialization of technological innovations
TEST
Toxicity Estimation Software Tool

• **PROBLEM:** There is a need to provide a reasonable estimate for toxicity values for a wide range of toxicological endpoints used for risk management tools

• **TECHNOLOGY SOLUTION:**
  - Toxicity can be estimated using Quantitative Structure Activity Relationship (QSAR) models
  - Developed a novel estimation technique based on hierarchical clustering methods
  - A user friendly software tool was developed to allow users to easily estimate the toxicity using QSAR models

• **CURRENT STATUS:** Version 3.2 of the software is available for download on the EPA website
  - TEST allows users to rapidly estimate acute aquatic toxicity, acute mammalian toxicity, and mutagenicity
  - TEST is being used by users all over the world

http://www.epa.gov/nrmrl/std/cppb/qsar/index.html
WAR (WAste Reduction Algorithm)

- **PROBLEM:** There is a need to be able to identify and evaluate environmental concerns of chemical manufacturing processes. There is also a need to educate professionals so that they will consider environmental issues when evaluating the performance of these processes.

- **TECHNOLOGY SOLUTION:**
  - The WAR GUI software allows users to enter chemical process data and then estimate the potential environmental impact.
  - The software allows the users to compare several different process designs using several different environmental impact categories.

- **CURRENT STATUS:** Version 1.0.17 of the software is available for download on the EPA website.
  - WAR is being used as an educational tool worldwide (researchers from 50 different countries have downloaded it).

http://www.epa.gov/nrmrl/std/cppb/war/sim_war.htm
## Types of Environmental Impacts Evaluated in the WAR Algorithm

<table>
<thead>
<tr>
<th>General Impact Category</th>
<th>Impact Category</th>
<th>Measure of Impact Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>Human Toxicity</td>
<td>Ingestion</td>
<td>Lethal Dose (50%) - LD&lt;sub&gt;50&lt;/sub&gt;</td>
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<tr>
<td></td>
<td>Inhalation/Dermal</td>
<td>OSHA PEL</td>
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<tr>
<td>Ecological Toxicity</td>
<td>Aquatic Toxicity</td>
<td>Fathead Minnow LC&lt;sub&gt;50&lt;/sub&gt;</td>
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<tr>
<td></td>
<td>Terrestrial Toxicity</td>
<td>LD&lt;sub&gt;50&lt;/sub&gt;</td>
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<tr>
<td>Global Atmospheric Impacts</td>
<td>Global Warming Potential</td>
<td>GWP</td>
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<td></td>
<td>Ozone Depletion Potential</td>
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<tr>
<td>Regional Atmospheric Impacts</td>
<td>Acidification Potential</td>
<td>AP</td>
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<td></td>
<td>Photochemical Oxidation Potential</td>
<td>PCOP</td>
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PARIS II
Program to Assist the Replacement of Industrial Solvents

• PROBLEM:
Solvents used by industry are often hazardous and can cause significant environmental impact.

• TECHNOLOGY SOLUTION:
  – EPA’s PARIS II software finds less harmful solvents or solvent mixtures to replace the more hazardous solvents.
  – The replacement solvents or solvent mixtures have similar physical and chemical properties as the original solvents.
  – The replacement solvents or solvent mixtures are less hazardous.

• CURRENT STATUS:
The PARIS II software is available for internal EPA use.
Green Chemistry
Catalytic Ozone Technology

• **Problem:** Large amount of volatile organic (methanol) and sulfur compounds are released to the environment every year
  – Current technologies such as Incineration, thermal combustion are energy intensive, not economical, and generate NOx, SOx

• **Solution**
  – Technology highly effective at industrial scale tests
  – Methanol converted to methyl formate (less 250 °C)
  – Complete removal of sulfur containing air pollutants

• **Status:** Collaboration with at Domtar Pulp Mill, Hawesville, KY for further tests
Green Chemistry
Membrane Assisted Vapor Stripping for Efficient Biofuel Production

• **PROBLEM:** Conventional separation of dilute alcohol-water mixtures in biofuel production is energy inefficient

• **TECHNOLOGY SOLUTION:**
  – hybrid process integrating vapor stripping, vapor compression, and vapor permeation membrane operations
    • enables the efficient recovery of process heat
    – >50% energy savings experimentally verified

• **CURRENT STATUS:**
  – developed in collaboration with US membrane company
    • US and International patents pending
    • end-user tests in progress
  – exploring process enhancements and application to other energy-intensive separation challenges
Nanotechnology

• **PROBLEM:** As materials, composites and products based on nanotechnology are developed and enter the marketplace, there exists a need to evaluate their potential environmental impact across the entire life cycle.

• **TECHNOLOGY SOLUTION:**
  – Applying a holistic approach towards the design, manufacture, use and disposal of these materials.
  – Development of new methodologies for these materials and performing Life Cycle Inventories Assessments (Ag, Li and CNTs).
  – Utilizing Green Chemistry to design environmentally friendly nanomaterials
  – Understanding the link between the physical properties of nanomaterials and their interaction with the environment.

• **CURRENT STATUS:** Continued in-house directed research in the area of method development, synthesis, physical characterization and application of nanomaterials. Also, beginning to have increased industrial participation.
Solar Nanocatalytic Technology for Water Treatment

- **Problem:**
  - Large volumes of water contaminated with man-made pollutants, pesticides, dye, pharmaceuticals, MTBE, solvents

- **Solution:**
  - Novel process Uses nano-photocatalyst and solar energy for the treatment of ground and surface waters
  - Can remove the organic compounds and also replace a chlorination disinfection step as a tertiary treatment
  - Process is an economical green approach

- **Status:**
  - Technology tested successful at bench scale,
  - Should be developed further looking at water quality objectives of technical reliability and economic and environmental sustainability.
**PROBLEM:** Synthesize nanomaterials in a sustainable manner.

**TECHNOLOGY SOLUTION:** *Learning from Nature*- Use Vitamin B$_1$ in water to do the reduction and capping.

**CURRENT STATUS:** Aligned palladium nanoplates synthesized and toxic reducing and capping agents avoided.

_Nadagouda, Polshettiwar & Varma: J. Mat. Chem., 19, 2026 (2009)_
PROBLEM: Green’ synthesis of nanoparticles using biorenewable sources.

TECHNOLOGY SOLUTION: Utilize source of polyphenols from agricultural waste.

CURRENT STATUS: ‘Rags to riches’ story of nanoparticle generation using red wine and red grape pomace.

Green Remediation

**PROBLEM:** There are ~ 500,000 contaminated sites across the USA. Current cleanup technology requires excavation and may even generate toxic by-products. Remediating various environmental toxins in the subsurface and in water at or around these sites is a complex challenge.

**TECHNOLOGY SOLUTION:** Through a CRADA (445-08) between EPA’s National Risk Management Research Laboratory (NRMRL) and the private company VeruTEK in Bloomfield, Connecticut, EPA green-synthesis technology is being used to further improve VeruTEK’s green remediation and treatment technologies used in environmental cleanup. This project combines EPA’s expertise in green synthesis of nanoparticles with VeruTEK’s expertise with surfactant enhanced in situ chemical oxidation and reduction methods. The benefits from the new green-synthesis methods over conventionally used processes are: only natural materials are used; no hazardous waste is produced; reduced processing is required; materials are more stable, easily stored, and transported; and, materials can be more easily produced around the world.

**Current Status:**
Demonstrated destruction of contaminated soils

Remediation Application: *J. Mater. Chem. 19, 8671 (2009)*;
Toxicity studies: *Green Chemistry, 12, 114 (2010)*-Hot Article
No Organic Solvent—
Even in the Work-Up Step

Reaction in Pure Aqueous Medium
Development of a Technology - Sorbster®

• Jointly developed, protected technology under CRADA (#192A-00)

• Intellectual property portfolio; EPA is an assignee
  • Provisional patent filed April 2009
  • International Patents (applied); China, India, Canada and Japan
  • EPA has issued an exclusive worldwide license to MAR Systems

• Target Market - Drinking Water
  – US Market – 13 Million people
  – Global Market – 100 Million people

• Other Markets:
  – Industrial Water Discharge Treatment
  – Mining Runoff
  – Coal and Incinerator Stack Gas (incl. mercury)
  – Industrial Ecology

• Market Penetration
  – Strategic Partnerships
  – Low cost, ‘Home Depot’ Solution

MAR Systems Named by Business Week as One of ‘America’s Most Promising Start-ups’; January 2011.
Green Chemistry Is About Innovation, Understanding Impacts &........

- Waste
- Materials
- Hazard
- Risk
- Energy
- Environmental Impact
- COST
Innovating on Innovation......
Thank You

Look for our publications.......