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Upcoming ACS GCI Webinar!

Nanomaterial Design Guided by the Principles of Green Chemistry

Thursday, May 18 @ 2:30pm ET

How can green chemistry be applied to nanotechnology to achieve the high-performance needed for advanced applications while preventing or reducing health and environmental impacts? Join James Hutchison from the University of Oregon as he discusses the foundations for greener nanotechnology and presents a case study that uses nanomaterial product innovation guided by green chemistry.

What You Will Learn

- The opportunity to achieve a net environmental benefit by bringing together green chemistry with nanoscience
- The role that green chemistry plays in designing high-performance nanomaterials and efficient nanomaterial production
- How green chemistry and nanoscience can be used together to develop innovative new products with environmental benefits

Thursday, April 13, 2017

**The Good, The Bad and the Uncertain: Public Perception of the Chemical Enterprise**
Session 3 of the Industry Science Series

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Sustainability Challenges of the Textiles, Dyeing and Finishing Industries: Opportunities for Innovation

Dr. Richard Blackburn
Sustainable Materials Research Group
University of Leeds
@RichardBlackb18

Which is the most sustainable textile fibre?

Cotton  Polyester  Wool  Nylon

Polyester image By Bearas [Own work] [CC BY-SA 4.0 (http://creativecommons.org/licenses/by-sa/4.0)], via Wikimedia Commons
Wool image By 4028mdk09 [Own work] [CC BY-SA 3.0 (http://creativecommons.org/licenses/by-sa/3.0)], via Wikimedia Commons
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Necessity for Sustainable Products

- 2012 - world population 7 billion
- 2050 - expected to rise to over 9 billion
- Increases demand
  - food, energy, water, resources, chemicals
- Increases environmental burden
  - pollution
  - depletion of finite non-renewable resources (e.g. fossil fuels)

- Synthetic chemical products and processes afford a significant improvement in quality of life
- Growing middle class want these consumer products too

Synthetic Fibre Revolution

20th Century polymers
- nylon, 1935
- polyurethane, 1937
- polyester: Terylene, 1941; Dacron, 1946
- acrylic, 1944
- polypropylene and HDPE, 1951
Synthetic Fibre Sustainability Challenges

- Non-degradable, non-renewable

- But, polyester highest share of textile market
  - >50m tpa

- Raw materials for fibres must change

- Recyclable – mechanical or chemical?

Sustainability Considerations

- RAW MATERIALS
- ENERGY
- WATER
- EMISSIONS
Public Perception

• Demand (and rejection) for consumer products can be driven by the public and the media
  • “Biodegradable”, “Natural”, “Organic”
    • perceived by the public to be good for the environment
  • “Synthetic”, “Non-organic”, “GM”
    • perceived by the public to be bad for the environment
  • “Chemistry”
    • Public perception of science…
• Do the public understand what “Sustainable” means?

Ideal Sustainable Product

• Provide an equivalent function to the product it replaces
• Performs as well as or better than the existing product
• Is designed to be desirable
• Be available at a competitive or lower price
• Have a minimum environmental footprint for all the processes involved
• Be manufactured from renewable resources
• Use only ingredients that are safe to both humans and the environment
• No negative impact on food supply or water
Textile Dyeing Processes

- Traditional dyeing processes use 5.8 trillion litres water p.a.
  - ~3.7 billion Olympic swimming pools
- 10-20% dye remains after dyeing (plus other chemicals), leaving potential for wastewater pollution
  - One fifth of the world's industrial water pollution (World Bank)
- 391 billion kWh energy for dyeing processes
- Innovative technologies needed to reduce, or eliminate, water, energy and auxiliary chemicals in dyeing

Treatment of Textile Dyeing Effluent

- Wastewater from dyeing processes one of biggest contributors to textile effluent
- Mainly residual dyes and auxiliary chemicals
- >50,000 tpa dye discharged into effluent

<table>
<thead>
<tr>
<th>Dye Class</th>
<th>Fibre</th>
<th>Loss to Effluent (% applied)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acid</td>
<td>polyamide (nylon)</td>
<td>5-20</td>
</tr>
<tr>
<td>basic</td>
<td>acrylic</td>
<td>0-5</td>
</tr>
<tr>
<td>direct</td>
<td>cotton</td>
<td>5-30</td>
</tr>
<tr>
<td>disperse</td>
<td>polyester</td>
<td>0-10</td>
</tr>
<tr>
<td>metal-complex</td>
<td>wool/polyamide</td>
<td>2-10</td>
</tr>
<tr>
<td>reactive</td>
<td>cotton</td>
<td>10-50</td>
</tr>
<tr>
<td>sulphur</td>
<td>cotton</td>
<td>10-40</td>
</tr>
<tr>
<td>vat</td>
<td>cotton</td>
<td>5-20</td>
</tr>
</tbody>
</table>
Treatment of Textile Dyeing Effluent

- Dyeing effluent in a watercourse aesthetically undesirable, but has a more serious environmental impact
- High BOD combined with spectral absorption of dye
  - Can affect photosynthetic processes
  - Reduction in $O_2$ levels in water $\rightarrow$ suffocation of aquatic flora and fauna
- Dyestuffs may be also have aquatic toxicity (metals, AOX)
- Several methods developed to remove colour from effluent
- Varying in effectiveness, economic cost, and environmental impact (of the treatment process itself)


Polyester Dyeing Process

- Hydrophobic fibre dyed with hydrophobic disperse dye
- Traditional aqueous process requires dispersing agents/surfactants and high temperatures (typically 130 °C) under pressure
- Other dyeing auxiliaries often required
- Large amount of waste dye left over in effluent
- Surface dye removed with surfactants and/or reducing agents
- Innovation in scCO$_2$ dyeing to completely change polyester dyeing process
**scCO₂ dyeing**

System comparison with traditional polyester dyeing

<table>
<thead>
<tr>
<th>WATER</th>
<th>Zero water used</th>
</tr>
</thead>
<tbody>
<tr>
<td>PROCESS</td>
<td>No auxiliary chemicals</td>
</tr>
<tr>
<td>WASTEWATER</td>
<td>Nearly 100% dye used in process. Zero waste</td>
</tr>
<tr>
<td>FOOTPRINT</td>
<td>¼ of physical footprint to dye same mass of fabric</td>
</tr>
<tr>
<td>ENERGY</td>
<td>Reduces energy consumption by 63%</td>
</tr>
<tr>
<td>EFFICIENCY</td>
<td>40% faster than traditional dyeing processes</td>
</tr>
</tbody>
</table>

**scCO₂ dyeing - limitations**

- Machines are more expensive than traditional water-dyeing machines
  - “costs will come down through scale and lower water and energy expenses“
- Only works on polyester fabrics and can’t be used to dye cotton
  - Cotton makes up about 35% global fibre market
  - Some relatively unsuccessful work on modifying cotton
- Significant opportunity to develop low or zero water dyeing systems for coloration of cellulosics
Coloration of Cotton

- Dyeing of cotton primarily conducted using reactive dyes
- Despite development of dyes with high fixation, dyeing still uses high quantities of salt, water (and energy), and creates colour pollution

- Soil too alkaline to support crops
- Kills aquatic life
- Fresh watercourses turned saline downstream from dyehouses
- Difficult to remove from effluent

Wash-off of Reactive Dyeings on Cotton

- Dye transfer inhibiting (DTI) polymers (used in laundry detergents) were employed to remove unfixed dyes
- Much more efficient, economical and sustainable process developed
- Significantly reduces operation time, water consumption and energy consumption
  - poly(vinylpyridine-N-oxide) polymers were the most effective
  - poly(vinylpyridine betaine) polymers also highly efficient

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Time (min)</th>
<th>Water (L/kg fabric)</th>
<th>Energy (MJ/kg fabric)</th>
</tr>
</thead>
<tbody>
<tr>
<td>recommended wash-off</td>
<td>250</td>
<td>60</td>
<td>9.21</td>
</tr>
<tr>
<td>DTI wash-off</td>
<td>50</td>
<td>30</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Bigger Problems with Cotton

• **NATURAL doesn’t necessarily mean sustainable**
• Cotton production >25 million tpa
• High levels of pesticides (25% world total)
• High levels of insecticides (11% world total)
• Very high irrigation levels
  • 1 kg of cotton fibre requires 20,000-40,000 L
  • Water average person consumes in a lifetime
• Only grows in certain climates
  • Deforestation to grow cotton
• High area of land for mass of useable fibre

Sustainable Cotton?

**Organic cotton**

• Widely promoted as the answer to cotton’s problems
• Global production (in over 20 countries, mainly India) only 1.1% of world cotton production
• No genetically modified seed permitted
• No herbicides or pesticides
• Ethical labour employment standards
• Requires approximately 1.4x area of land to produce same mass of fibre
• Still has very high water consumption
• Not a viable alternative on a global scale to completely replace non-organic cotton
Sustainable Cotton?

Better cotton

- GM pest-resistant strain referred to as ‘Bt cotton’
  - Naturally occurring protein (used by organic gardeners) – kills bollworm pests (moth larva)
  - Reduces pesticide sprays from 5 sprays to 0
  - Poisoning of workers virtually eliminated
  - More productive, particularly in India
  - Bt cotton is regarded as less ‘natural’
  - Cannot be classed as ‘organic’

- Better Cotton Initiative (BCI) set up to foster improvements in the sustainability of cotton production methods

Alternative Sustainable Cellulosic Fibres

Bast Fibres

- From stem of plants (flax, hemp, jute, ramie, nettle, kenaf, abaca)
- Plants with opportunities for performance fibres (e.g. Himalayan nettle)


- Processing to separate ultimate fibres is of concern
- Opportunities for innovation into alternative separation techniques (e.g. enzyme-assisted technologies)

**TENCEL® (lyocell) – Most Sustainable Fibre Production Process**

- Regenerated cellulosics made from trees
- Lenzing manufactures lyocell

![Diagram of wood pulp to Tencel® process]

- Wood from certified forests
- Direct closed-loop dissolution process
- $N$-methylmorpholine-$N$-oxide (NMMO)
- >99% recovery of solvent


**Green Footprint vs. Cotton**

- More than 50% of Lenzing’s fuel consumption sourced from renewable resource

![Graph comparing water consumption and environmental impact of production]
• New Lenzing fibre manufactured from industry waste, both cotton and lyocell

• Made from pulp that contains cotton scraps left over from cutting operations

Which textile fibre is lightweight and breathable, cool in the heat, warm in the cold, carries away moisture, has excellent odour management properties and a low carbon footprint?

Cotton  Polyester  Wool  Nylon
• Designing environmentally friendly and comfortable footwear

• Wool Runner – minimalist sneaker made of superfine New Zealand merino wool

Best Way to Mix Colours?

Nano-level

• Mixture of different dye molecules in dyebath to create desired shade

Micro-level

• Mixture of different dyed fibres in yarn formation process to create desired shade
Does Fibre Coloration Have to be Through Dyeing?

- **Dope-dyeing**: incorporation of colorant into spinning process
- Lyocell process makes this possible for cellulosics

**DyeCat Process**

- Catalytic process that allows colour to be integrated directly into polyesters
- Eliminates need for conventional dyeing
- Colour in fibre is generated at the same time the polymer is made
- Colours ‘locked into’ fibre providing a technically superior product
- No need for wasteful dyeing processes
- **DyeCat poly(lactic acid) fibre**
  - Renewable
  - Technically superior
  - Saves chemicals and energy
### DyeCat Process

- Coloration of polymer during synthesis
- Demonstrated on PLA using coloured catalysts


### Novel, Sustainable and Cost-Effective Textile Dyeing using Nanocellulosic Fibres

- Dr. Yunsang Kim *et al.*, University of Georgia
- Innovative dyeing processes using coloured nanocellulose
  - nano-sized cellulose fibrils (wood pulp) + dye → dyed nanocellulose dispersion
- Apply dyed nanocellulose dispersion onto the textile material using low water process
- Coloured nanocellulose permanently binds to textile surface
- Greatly reduces energy and water needed
Criticism of Chemistry use for Repellency in Outdoor Apparel

- Durable water repellents (DWR) applied to textiles to impart repellent functionality from water and oil
- For the last 60 years, per- and polyfluoroalkyl substances (PFASs) used in textile finishing
- Outdoor apparel industry has been directly targeted by Greenpeace
- The industry’s PFAS use has been discussed in three reports since 2012
- However, ratio of PFAS use in the outdoor apparel industry compared to whole textile industry unknown

“...significant adverse effects have not been found in the general human population, however, significant adverse effects have been identified in laboratory animals and wildlife”

Significant Attention to Alternative Chemistries

Suitable for Requirements?

- Mixed opinions on outdoor apparel requirements
- Involves wide range of activities, varying weather conditions, and demands on the wearer
- ‘Wetting’ of the fabric can cause detrimental cooling of the wearer – ‘life protection’
- Re-evaluation of consumer requirements

<table>
<thead>
<tr>
<th>Surface terminal groups</th>
<th>Critical surface tension $\gamma_c$ (mN/m) at 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CF₃</td>
<td>6</td>
</tr>
<tr>
<td>-CF₂</td>
<td>18</td>
</tr>
<tr>
<td>-CH₃</td>
<td>22</td>
</tr>
<tr>
<td>-CH₂</td>
<td>31</td>
</tr>
</tbody>
</table>

Silicones  Hydrocarbons  Dendritic/hyper-branched chemistry  Wax-based repellents
Move to Fluorine-Free: Sufficient Functionality?

Characterisation of repellent fabrics currently in use from a number of brands

喷雾测试 BS EN ISO 4920
行业标准用于测试表面湿润抗性

Fast Fashion

- 快速，低价格和一次性“超市”服装
- 对服装的需求将在2025年翻倍
- 环境影响
  - 美国进口超过10亿件服装，仅来自中国
  - 80%的纺织品运往垃圾填埋场（每年5000万吨）
  - 纺织业造成的环境损害激增
  - 安全性在不断削减成本的供应链中受到威胁
- 人类灾难
  (例如：Rana Plaza, 孟加拉国 - 1,100人死亡，2,500人受伤)
- 人类必须从零售商和消费者的头脑和态度做出巨大的改变

7m吨服装在英国每10分钟被扔掉

7m吨衣服在英国每10分钟被丢弃

Sustainable Textiles

- Greater use of sustainable raw materials
- Lower energy & water consumption and pollution generation in production
- Lower impact in use
  - Water, energy, chemicals in cleaning/laundering
- Design for easy disassembly/disposal/ recycling

**DESIGN FOR REDUCED CONSUMPTION AND LONGER LIFE**

- ‘Disposable’ products unsustainable

---

Which is the most sustainable textile fibre?

- Cotton
- Polyester
- Something else
Sustainability Challenges for the Textiles Industry

- Sustainability issues in the textiles industry have often been tackled in industry by tinkering and incremental change.

- Step-change solutions are needed to bring about truly sustainable apparel and footwear products.

Further Reading...
Thank you

Dr. Richard S. Blackburn
r.s.blackburn@leeds.ac.uk
@RichardBlackb18

“Sustainability Challenges of the Textiles, Dyeing and Finishing Industries: Opportunities for Innovation”

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