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ASIA PACIFIC

Perth waste plant leaches toxic PFAS into groundwater

2023-10-03

Damaged concrete has resulted in water contaminated with toxic chemicals leaching into groundwater in Perth's south, the state's environmental regulator says.

Waste management giant Cleanaway has been issued an environmental protection notice by the Department of Water and Environmental Regulation after PFAS chemicals were found in groundwater well above Australian guidelines next to its Henderson facility.

DWER compliance and enforcement director Ruth Dowd's notice was issued to Cleanaway last week after the company reported the discovery to DWER in its annual environmental report.

The notice contained a series of demands that the company investigate the discovery and come up with a plan to control or abate the issue within 60 days.

Cleanaway's Henderson facility treats wastewater from commercial and industrial customers in WA's south-west.

Read More

WA Today, 03-10-23

https://www.watoday.com.au/national/western-australia/toxic-pfas-leaches-into-groundwater-near-waste-management-facility-in-perth-s-south-20231002-p5e94k.html

Hearing for updates to cosmetics rules

2023-10-04

A public hearing to consider the proposed changes to the Cosmetic Products Group Standard was held on 20 September 2023.

The decision-making committee has adjourned the hearing and requested further information from the Ministry of Health regarding labelling of fluoride-containing toothpastes.

The amendments we are proposing include:

• banning all PFAS ingredients in cosmetic products

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- extending the group standard to cover more products
- aligning our rules for ingredients with the European Union.

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EPA New Zealand, 04-10-23

https://www.epa.govt.nz/public-consultations/in-progress/updates-to-the-cosmetic-products-group-standard/

Hydrofluorocarbons decision on special import permits to come

2023-10-04

Our decision on how new bulk hydrofluorocarbons (HFCs) will be allocated in 2024 is expected later this month.

HFCs are a group of harmful greenhouse gases used in heat pumps, air conditioning and refrigeration. They have a global warming potential more than 50 times higher than carbon dioxide.

We have been reducing the limit for importing these gases every two years, in line with Ozone Layer Protection Regulations. We will reduce the import limits again in 2025.

This year we received 14 applications from wholesalers and individual businesses, requesting more than three times the amount available for allocation.

Read More

EPA New Zealand, 04-10-23

https://www.epa.govt.nz/industry-areas/hazardous-substances/hfcs/types-of-permit/

Have your say on Emesto Prime fungicide

2023-10-04

There is still time to provide feedback on an application by Bayer New Zealand Limited to import or manufacture the fungicide Emesto Prime.

The substance is used on potatoes to control a soil fungus and contains the active ingredient penflufen, which is new to Aotearoa New Zealand.

Penflufen has been approved in countries including Australia, Canada, Japan, and the United States of America.



We are particularly interested in potential effects of the substance not yet identified, potential impacts on Māori wellbeing, rights, and interests, and issues experienced by anyone involved in or affected by the potato industry.

Submissions close at midnight on 17 October 2023.

Read More

EPA New Zealand, 04-10-23

https://www.epa.govt.nz/public-consultations/open-consultations/application-to-introduce-a-new-fungicide-for-potatoes/

PFAS are forever – a complicated chemical family

2023-10-04

Commonly called forever chemicals, PFAS are a large, complex group of synthetic chemicals that are used widely in consumer products and industrial processes around the world for their water, grease, heat and stain-resistant properties.

While many PFAS may not be known to have health impacts, the fact they are persistent and can accumulate in our bodies means more information is needed.

We take a precautionary approach to regulating these chemicals and have already taken action in some areas:

- phasing out all firefighting foams containing PFAS
- proposing a ban on all PFAS in cosmetic products
- testing for background levels of PFAS in the New Zealand environment. Dr Peter Dawson (Principal Scientist, Hazardous Substances) explains what per- and polyfluoroalkyl substances (PFAS) are, how they are used, and the

per- and polyfluoroalkyl substances (PFAS) are, how they are used, and global and national response to potential risks from these chemicals.

Read More

EPA New Zealand, 04-10-23

https://www.epa.govt.nz/community-involvement/science-at-work/pfas/



Recent EPA decisions

2023-10-04

OCT. 13, 2023

Containment

APP204680by Plant & Food Research to import or manufacture Natural product (NP) soft chemistries to control diseases in containment. Approved with controls 21/09/2023.

APP204681by Plant & Food Research to import or manufacture soft alternatives for disease control in peas and beans in containment. Approved with controls 14/09/2023.

APP204685by Agronaturalis Ltd to import or manufacture ANL-F004 in containment. Approved with controls 15/09/2023.

APP204667by Adama New Zealand Limited to import or manufacture Adama experimental compounds in containment. Approved with controls 20/09/2023.

APP204687by Corteva AgriScience New Zealand Limited (formally known as DOW Agrosciences) to import or manufacture Experimental pesticides (11) in containment. Approved with controls 20/09/2023.

APP204701by Adama New Zealand Limited to import or manufacture Adama experimental fungicide compound in containment. Approved with controls 28/09/2023.

Insecticide

APP204033by Sustainable Agro Solutions to import or manufacture Coda Klean for release. Approved with controls 15/09/2023.

APP204592by Grosafe Chemicals Limited to import or manufacture Emulsifiable concentrate containing azadirachtin 10 g/L and neem oil 300 g/L for release. Approved with controls 11/09/2023.

Statutory determination

APP204519by Nufarm Limited to determine if NUN2299 is hazardous. Determined to be hazardous 31/08/2023.

Amendments to approvals

APP204671by FMC New Zealand Limited to amend DuPont Coragen Insecticide (HSR007969approved under HSR07132) under section 67A of

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the HSNO Act. Decided on 12 September 2023. The approval for DuPont Coragen Insecticide was amended to include the original maximum application rate control and reference that the reassessed maximum application rate is specific for use on turf.

APP204414by Environmental Protection Authority to amend methyl bromide (HSR001635reassessed under APP203660) under section 67A of the HSNO Act. Decided on 21 September 2023. The decision report was amended to correct a technical error in the classification table.

APP204636by Environmental Protection Authority to amend AGPRO Glyphosate Dry 800 WSG (HSR100815approved under APP201689) under section 67A of the HSNO Act. Decided on 21 September 2023. The approval for was amended to correct an error in the hazard classification.

APP204638by Environmental Protection Authority to amend paraquat (HSR003041reassessed under APP203301) under section 67A of the HSNO Act. Decided on 21 September 2023. The approval for was amended to correct an error in the hazard classification.

Read More

EPA New Zealand, 04-10-23

https://www.epa.govt.nz/industry-areas/hazardous-substances/chemical-reassessment-programme/amendments-to-approvals/

AMERICA

U.S. CPSC PUBLISHES DIRECT FINAL RULE IN FEDERAL REGISTER FOR 16 CFR PART 1263: SAFETY STANDARD FOR BUTTON CELL OR COIN BATTERIES AND CONSUMER PRODUCTS CONTAINING SUCH BATTERIES

2023-09-22

On September 21, 2023 the U.S. Consumer Product Safety Commission (CPSC) published a mandatory performance standard for Button Cell or Coin Batteries in the Federal Register. The Commission is publishing this determination, as required by Reese's Law, as well as a direct final rule to incorporate the voluntary standard by reference into the regulations. Consumer products subject to performance requirements in this direct final rule must be tested and certified as compliant with the direct final rule.

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As required by Reese's Law, to eliminate or adequately reduce the risk of injury from ingestion of button cell or coin batteries by children 6 years old and younger, CPSC approved a rule to establish requirements for button cell or coin batteries. The direct final rule is effective October 23, 2023, unless the Commission receives a significant adverse comment by October 5, 2023. If the Commission receives such a comment, they will publish a document in the Federal Register withdrawing this direct final rule before its effective date. Otherwise, in recognition of limited testing availability and for the avoidance of hardship, the Commission is granting a 180-day transitional period of enforcement discretion from September 21, 2023, through March 19, 2024.

Read More

OCT. 13, 2023

Bureau Veritas, 22-09-23

https://www.cps.bureauveritas.com/newsroom/us-cpsc-publishes-direct-final-rule-federal-register-16-cfr-part-1263-safety-standard

New Required Reporting on PFAS Defines New Regulatory Environment

2023-10-03

Companies will need to comply with new rule in 18 months, highlighting a quicker timeline.

There was a time when time itself was something offered to companies to help them comply with new regulations. Well, that time is over.

A myriad of factors resulted in an announcement by the EPA on Sept. 29 that manufacturers are now required to report on the presence of 1,462 PFAS chemicals in their processes and products. And this reporting will need to go back 12 years.

Information related to chemical identity, uses, volumes made and processed, byproducts, environmental and health effects, worker exposure, and disposal needs to be reported. Specifically these changes are being made to the Toxic Substances Control Act (TSCA) in Section 8 (a) (7) Reporting and Recordkeeping Requirements for PFAS chemicals.

The timeline for manufacturers to comply with this final rule is 18 months, with an additional six months for reports from small businesses that are solely reporting data on importing PFAS contained in products.



That timeframe is particularly quick given the very complex nature of PFAS as they are spread out far and wide in most companies' supply chains and serve a variety of functions.

Read More

EHS Today, 03-10-23

https://www.ehstoday.com/members/article/21274730/new-required-reporting-on-pfas-defines-new-regulatory-environment

Texas sues EPA over emissions standards

2023-10-02

The Texas Attorney General's Office is leading a challenge to the Environmental Protection Agency's pollution standards for cars and light-duty trucks in a lawsuit that could have a lasting impact on the automotive industry and the Texas power grid.

The latest: The U.S. Court of Appeals for the D.C. Circuit recently heard arguments in the case.

Why it matters: The lawsuit could determine how much the EPA can regulate the auto industry — and the results could have a drastic impact on air quality across the country.

• Transportation accounts for 28% of all greenhouse gas emissions in the U.S., according to the EPA — more than any other industry.

The big picture: A 2021 revision to the Clean Air Act requires the EPA to set vehicle emissions standards for cars and trucks manufactured between 2023 and 2026.

 Fifteen states — led by Texas and supported by advocates for the oil and gas industry — are challenging the rule, arguing it could affect the reliability of power grids and national security.

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Axios Dallas, 02-10-23

https://www.axios.com/local/dallas/2023/10/02/texas-sues-eta-pollution-cars-trucks-gas



EUROPE

Commission welcomes agreement on new legislation to prevent 500 million tonnes of emissions from fluorinated gases and ozone depleting substances

202310-05

The Commission welcomes the provisional agreement reached today by the European Parliament and the Council on strengthened rules to massively reduce greenhouse gas (GHG) emissions from fluorinated gases (F-gases) and ozone-depleting substances (ODS). Building on existing EU legislation which has already limited the use and emissions of these gases significantly, the Regulations agreed today will prevent almost 500 million tonnes of further emissions by 2050. It will contribute to the EU's 2030 climate targets of at least 55% emission reductions, and help make Europe climate-neutral by 2050.

Used in everyday life appliances, for example in refrigeration and air conditioning, F-gases and ODS are highly potent, human-made greenhouse gases with some of the worst global warming potential, often several thousand times stronger than carbon dioxide (CO2). The Regulation provides incentives to use climate-friendly alternatives, further stimulating the global market and helping other countries to make the transition as well. The world market for equipment using F-gases is currently growing rapidly due to increasing temperatures and higher living standards. The new Regulations contribute towards limiting global temperature rise in line with the Paris Agreement, and set an example internationally, raising ambition considerably beyond the Kigali amendment of the Montreal Protocol.

New F-gas Regulation

At EU level, F-gases currently account for 2.5 % of total GHG emissions. The reinforced F-gases Regulation will prevent the emission of around 300 million tonnes of CO2 equivalent by 2050.

 Delivering higher ambition: The agreement tightens the quota system for hydrofluorocarbons (HFC phase-down). The use of Hydrofluorocarbons (HFCs) - the most commonly used F-gases representing around 90% of F-gas emissions - would be reduced by 95% by 2030 compared to 2015, going down to zero by 2050. From 2025, the HFC quota that the Commission allocates every year will be sold for €3 per tonne of CO2 equivalent.

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- Restricting use, based on best practice: The agreement introduces new restrictions to make sure that F-gases are only used in new equipment where no suitable alternatives are available or that only the most climate-friendly F-gases are used. For example, new airconditioning, heat pumps and electrical equipment must use the most climate-friendly gases and some types of equipment must become F-gas free. For instance, in medium-voltage switchgear, where sulphur hexafluoride (SF6), the most potent greenhouse gas in the world, has been traditionally used. The new restrictions will apply from 2025 to 2035 depending on the readiness to shift to climate-friendly solutions for each type of equipment.
- Bringing positive impact at global level: In addition to promoting
 markets for climate-friendly equipment, an export ban will ensure that
 obsolete equipment using refrigerants with a high global warming
 potential that may not be sold in the EU can also not be exported to
 other countries in the world.
- Ensuring compliance with the Montreal Protocol: The F-gas proposal makes sure that the EU complies with all rules of the Montreal Protocol, and even goes beyond its ambition.
- Cutting costs for consumers: As the market for climate-friendly equipment expands, prices are expected to go down. Moreover, such equipment will generate lower energy costs, thus enabling people to save money over the lifetime of the equipment.

Read More

European Commission, 05-10-23

https://ec.europa.eu/commission/presscorner/detail/en/ip 23 4781

JRC weighs in on PPWR reusable packaging debate

2023-10-06

On September 25, 2023, the Joint Research Centre (JRC) of the European Commission presented findings from a study delving into the environmental impacts of single-use versus multiple-use packaging products as part of the ongoing discussion over whether the Packaging and Packaging Waste Regulation (PPWR) should include reuse targets (FPF reported).

The JRC is the "science and knowledge service of the European Commission" meant to provide independent evidence to support EU policy development. The ongoing study, initiated in May 2023 and

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expected to run until November 2023, is focused on assessing the environmental performance of packaging for food and beverages. JRC researchers used a life cycle assessment-based approach to evaluate the environmental impacts from food contact article production to end-of-life. The assessments were grounded in broad array of data collection and analyses, including factors like the number of reuses, transport distances, energy mix, and end-of-life waste management. For each factor, JRC ran a sensitivity analysis to check assumptions and find how important a role each played in the final impact score.

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FPF, 06-10-23

https://www.foodpackagingforum.org/news/jrc-weighs-in-on-ppwr-reusable-packaging-debate

INTERNATIONAL

Civil society organizations introduce new certification program for reusable food packaging

202310-06

On September 12, 2023, nonprofit organizations Center for Environmental Health (CEH) and Clean Production Action (CPA) introduced a novel certification program aimed at reducing waste and eliminating hazardous chemicals associated with single use foodware materials in a press release. The so-called "GreenScreen Certified Standard for Reusable Food Packaging, Food Service Ware, and Cookware" addresses the growing demand among consumers for products that prioritize safe chemistry and reduce waste (FPF reported).

The standard focuses on many concerns associated with single-use foodware and cookware, including exposure to toxic chemicals, reusability, and material-specific concerns on post-consumer recycled content. The certification comes in three levels that are partially defined by the strictness with which an organization tests for known hazardous chemicals such as per- and polyfluoroalkyl substances (PFAS), bisphenols like BPA, and phthalates, which have been linked to kidney cancer, infertility, and ADHD, respectively (FPF reported, also here and here).

The standard outlines criteria for reusability with tests particularly focused on the long-term viability of the foodware. A product containing any

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plastic or polymer components "must maintain its shape, structure, and function after 780 cycles in a cleaning and sanitizing process." Testing to ensure that any recycled materials used in food packaging, service ware, cookware, and food containers do not contain known hazardous chemicals that can be introduced or concentrated in the recycling process must also be undertaken (FPF reported). Additionally, companies will have to confidentially share the full ingredient list of their products to obtain any certification.

Read More

FPF, 06-10-23

https://www.foodpackagingforum.org/news/civil-society-organizations-introduce-new-certification-program-for-reusable-food-packaging



REACH Update

OCT. 13, 2023

ECHA Publishes OEL Report for 1,3-Butadiene | Public Consultation

2023-09-29

OCT. 13, 2023

The European Chemicals Agency (ECHA) has released its scientific report for the evaluation of occupational exposure limits (OELs) for 1,3-butadiene, a chemical commonly used in industrial processes. This report is now open for public consultation until November 20, 2023. As part of the consultation process, parties are encouraged to provide their comments and suggestions regarding the proposed OELs for 1,3-butadiene. Feedback received during this period will be considered by the RAC in its decision-making process.

Link to ECHA Scientific report for evaluation of limit values for 1,3-butadiene at the workplace

Read More

Chemycal, 29-09-23

https://chemycal.com/news/89cefcbc-4d9e-482a-abec-4c79330a9842/ECHA_Publishes_OEL_Report_for_13-Butadiene__Public_Consultation

ECHA receives thousands of comments on PFAS restriction proposal

2023-10-02

More than 4,400 organisations, companies and individuals submitted comments and information on the proposal to restrict per- and polyfluoroalkyl substances (PFAS) in the European Economic Area.

As of 25 September, ECHA has received more than 5,600 comments from more than 4,400 organisations, companies and individuals regarding the PFAS restriction proposal.

ECHA states in an update that these comments will be checked by its scientific committees for Risk Assessment (RAC) and Socio-Economic Analysis (SEAC), and those providing relevant evidence-based information will be considered in the opinion-making process.

The five countries who prepared the initial proposal – namely Denmark, Germany, the Netherlands, Norway and Sweden – will also review the consultation input, which may lead to an update of their initial proposal based on it.



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Evertiq, 02-10-23

https://evertiq.com/news/54445

Microplastics

2023-10-06

Plastics make our lives easier in many ways and are often lighter or cost less than alternative materials. However, if they are not properly disposed of or recycled, they may end up in the environment where they stay for centuries and degrade into smaller and smaller pieces. These small pieces (typically smaller than 5mm) are called microplastics and they are of concern.

Microplastics are solid plastic particles composed of mixtures of polymers and functional additives. They may also contain residual impurities. Microplastics can be unintentionally formed when larger pieces of plastic, like car tyres or synthetic textiles, wear and tear. But they are also deliberately manufactured and added to products for specific purposes, such as exfoliating beads in facial or body scrubs.

Timetable for restriction of intentionally added microplastics

	Timing
Intention to prepare restriction dossier	17 January 2018
Call for evidence	1 March - 1 May 2018
Stakeholder workshop	30 - 31 May 2018
Submission of the Annex XV restriction dossier	11 January 2019
Consultation of the Annex XV dossier	20 March 2019 – 20 September 2019
RAC opinion	June 2020
Draft SEAC opinion	June 2020
Consultation on draft SEAC opinion	1 July - 1 September 2020
Combined final opinion submitted to the Commission	February 2021
Draft amendment to the Annex XVII (draft restriction) by Commission	30 August 2022
Discussions with Member State authorities and vote	2022-2023, voted on 27 April 2023

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	Timing
Scrutiny by Council and European Parliament	Before adoption (3 months)
Restriction adopted	25 September 2023

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ECHA, 06-10-23

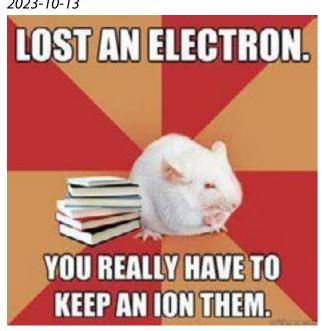
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Janet's Corner

Lost an Electron

2023-10-13





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Hazard Alert

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Nitrobenzene

2023-05-12

OCT. 13, 2023

USES [2,3]

The main use of Nitrobenzene is to make the important industrial chemical Aniline, which is used in the manufacture of plastics and rubbers, dyes, agrochemicals and petrol additives. Furthermore, nitrobenzene is used in shoe and floor polishes, leather dressings, paint solvents, and other materials to mask unpleasant odours. Redistilled, as oil of mirbane, nitrobenzene has been used as an inexpensive perfume for soaps. A significant merchant market for nitrobenzene is its use in the production of the analgesic paracetamol (also known as acetaminophen).

EXPOSURE SOURCES & ROUTES OF EXPOSURE [3]

Exposure Sources

Exposure can occur in the workplace during its manufacture, processing, and use, or in the environment following releases to air, water, land, and groundwater. Exposure can also occur when people use nitrobenzenecontaining paints and polishes.

Routes of Exposure

Nitrobenzene enters the body when people breathe air or consume food or water contaminated with nitrobenzene. It can also be absorbed through skin contact. It does not remain in the body due to its breakdown and removal.

HEALTH EFFECTS [4]

Acute Health Effects

Acute inhalation, oral, and dermal exposure to nitrobenzene in humans produces methemoglobinemia, in which haemoglobin (which carries oxygen in the blood) is converted to methemoglobin, resulting in lowering the amount of oxygen released to the tissues of the body. This lowered oxygen capacity is associated with fatigue, weakness, dyspnea, headache, and dizziness. At higher concentrations, depressed respiration, bluish-grey skin, disturbed vision, and coma may occur. Animal studies have reported methemoglobinemia and effects on the liver, kidney, spleen, and central nervous system (CNS) from acute inhalation exposure to nitrobenzene.

Nitrobenzene is an organic compound with the chemical formula C6H5NO2. It is a pale yellow oil with an almond-like odour. It freezes to give greenish-yellow crystals. [1] The solid crystals melt at 6 degrees celsius and the liquid boils at 211 degrees celsius. Nitrobenzene is flammable. It dissolves only slightly in water, but mixes well with most organic (carboncontaining) solvents. Nitrobenzene is one of a group of substances known as the volatile organic compounds (VOCs). [1,2]

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Tests involving acute exposure of rats have shown nitrobenzene to have moderate acute toxicity from oral exposure.

Carcinogenicity

EPA has classified nitrobenzene as a Group D, not classifiable as to human carcinogenicity.

Other Effects

No information is available on the reproductive or developmental effects of nitrobenzene in humans. Developmental effects, such as birth defects or embryotoxic effects, have not been reported in animal studies with inhalation exposure to nitrobenzene. However, reproductive effects, including a decrease in fertility, reduced testicular weights, and decreased sperm production have been noted in inhalation and oral animal studies.

SAFETY

First Aid Measures [5]

- Eye Contact: Check for and remove any contact lenses. Immediately flush eyes with running water for at least 15 minutes, keeping eyelids open. Cold water may be used. Do not use an eye ointment. Seek medical attention.
- **Skin Contact:** After contact with skin, wash immediately with plenty of water. Gently and thoroughly wash the contaminated skin with running water and non-abrasive soap. Be particularly careful to clean folds, crevices, creases and groin. Cover the irritated skin with an emollient. If irritation persists, seek medical attention. Wash contaminated clothing before reusing.
- Serious Skin Contact: Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek immediate medical attention.
- **Inhalation:** Allow the victim to rest in a well ventilated area. Seek immediate medical attention.
- **Serious Inhalation:** Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. Seek medical attention.
- **Ingestion:** Do not induce vomiting. Examine the lips and mouth to ascertain whether the tissues are damaged, a possible indication that the toxic material was ingested; the absence of such signs, however,

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is not conclusive. Loosen tight clothing such as a collar, tie, belt or waistband. If the victim is not breathing, perform mouth-to-mouth resuscitation. Seek immediate medical attention.

Workplace Controls & Practices [4]

Provide exhaust ventilation or other engineering controls to keep the airborne concentrations of vapours below their respective threshold limit value. Ensure that eyewash stations and safety showers are proximal to the work station location.

Personal Protective Equipment [5]

Gloves and Clothing

It is recommended that the following personal protective equipment be used when handling nitrobenzene:

- · Splash goggles;
- Lab coat;
- Vapour respirator (be sure to use an approved/certified respirator or equivalent);
- Gloves

Personal Protection in Case of a Large Spill:

- Splash goggles;
- · Full suit;
- Vapour respirator;
- Boots;
- Gloves;
- A self contained breathing apparatus should be used to avoid inhalation of the product.
- Note: Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

REGULATION

United States

EPA: The Environmental Protection Agency recommends that levels in lakes and streams should be limited to 17 parts of nitrobenzene per million parts of water (17 ppm) to prevent possible health effects from drinking water or eating fish contaminated with nitrobenzene. The EPA

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requires that discharges, spills, or accidental releases of 1,000 pounds or more of nitrobenzene must be reported to the EPA.

OSHA: The Occupational Safety and Health Administration has set a permissible exposure limit of 5 milligrams nitrobenzene per cubic metre of air (5 mg/m³) for an 8-hour workday in a 40-hour workweek.

ACGIH & NIOSH: The American Conference of Governmental and Industrial Hygienists and the National Institute for Occupational Safety and Health also recommend an occupational exposure limit of 5 mg/m³ for nitrobenzene.

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Material cycle for amine chemistry: Important building blocks created from platform chemical in single step

2023-10-11

A team of researchers at LIKAT, in cooperation with the Dalian Institute of Chemical Physics, has just presented such a catalyst in the journal Nature Communications. In a single reaction step, it allows the platform chemical furfural to be converted into amines, which are among the most important synthesis building blocks.

Amines are functional components in the synthesis of drugs and agrochemicals, and they are used en masse in many fields, such as energy technology and materials science. Ultimately, they introduce into chemical processes those nitrogen units that provide specific properties. The amine market is growing strongly, with estimates predicting annual growth rates of 8% over the next ten years.

Reaction without waste and by-products

This growth attracted Haifeng Qi from Dalian to take a closer look at this reaction in his dissertation. "Because amine synthesis is still largely dependent on fossil resources," he says. At the same time, interest is growing worldwide in cost-effective methods for their sustainable production based on renewable raw materials, explains Dr. Kathrin Junge, in whose research group Dr. Qi is currently working as a Humboldt Fellow at LIKAT, the Leibniz Institute for Catalysis in Rostock.

The new reaction proceeds in a single step, instead of the previous five to six steps. Qi uses the platform chemical furfural, which is produced entirely from biowaste, as well as ammonia and hydrogen. This produces the amine piperidine, an intermediate for pharmaceuticals, crop protection agents and solvents, among other things.

As a model reaction, this process can be used universally. "For example, if you further heat the product piperidine and at the same time turn off the supply of hydrogen and ammonia, another amine called pyridine is formed," Dr. Qi reports of his research. Both times he completely converted his starting materials, no waste products were formed.

Yield of almost 100%

This also means that the usual purification of the amines can be dispensed with after these processes, as Dr. Junge says. "The catalyst can also be easily reused for new cycles." Just how highly selective it is in controlling

Fossil raw materials still dominate the chemical industry. **But laboratories** around the world are researching ways in which large-scale processes can avoid crude oil, natural gas and coal in the future. **So-called platform** chemicals are gaining in importance; they are produced entirely from renewable raw materials. But their use in industrial processes requires special catalysts.



the reaction is shown by the yield, which is up to 97%. Basically, a sensational value.

How does the catalyst manage that? Dr. Qi smiles when he hears the question, because that's exactly what he also asked himself when he recognized its highly selective approach. That's why the catalyst was precisely examined in the analysis area of LIKAT.

Qi had prepared his catalyst from cobalt and ruthenium in the usual way for heterogeneous catalysis: He dissolved salts of the two metals in water, added a support material to which the metal could settle, then allowed the solvent to evaporate and the complex to dry. He then exposed his catalyst to a heat of 400°C. Chemists call this process pyrolysis: The material does not burn, but changes its structure.

Individual atoms cause the effect

How decisively the heat had changed the catalyst structure was later revealed under the high-tech microscopes. Dr. Junge explains, "Groups of cobalt atoms came together in nanoparticles, on whose surface the ruthenium was deposited, in the form of individual atoms."

Qi states, "It was exactly this single-atom structure, as we call it, that made the effect. And it's quite stable." All of this makes for a fairly simple arrangement for this amine production that Dr. Junge believes any lab technician could handle.

"Such a material cycle of amine production based on biomass is hardly known," emphasizes LIKAT Director Prof. Dr. Matthias Beller, who supervised Qi's work from the German side. This could be the basis of a "biorefinery of the future."

Phys Org, 11 October 2023

https://phys.org

You don't need coding to be a chemist

2023-02-06

At one time, most chemists would have at least needed rudimentary glassblowing skills. But since most of their glassware requirements were common to many thousands of other scientists, companies soon emerged to serve that market with off-the-shelf products. Today, it would be absurd to make your own Liebig condenser before you can carry out a distillation, or your own reagents or instruments for that matter.

Chemists will always need to adapt their skills to new ways of doing science. When I was an undergraduate, I was taught how to make melting point tubes by drawing out glass capillaries over a Bunsen burner flame. I remember this because I was really bad at it; the sharps bin was full of my handiwork. Thankfully, the exercise was already outdated even then and there was no need to test my manual dexterity beyond that. There is a modern trend in research skills that I feel is equally absurd: that it will be essential to learn coding for the future of science. This notion is currently doing the rounds as more science moves from in vitro to in silico. Coding is certainly useful, but it is not a prerequisite for doing science, any more than glassblowing. This notion is also unhelpful because it emphasises the wrong part of research: focusing on how to make something, rather than why to make it. Perhaps most importantly, it ignores the much more important need for data skills.

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On a need-to-code basis

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As R&D becomes more digital, there will be less hands-on lab work, the argument goes. In the lab of the future, routine practical tasks will be automated and researchers will instead spend their time coding those machines and their data workflows. Hence, we should send everyone on coding bootcamps.

I know a lot of scientists that love the idea of learning new digital skills, including coding – I'm one of them. I've learned enough to do useful things with coding at various times in my career. But only when I have had to.

Recently, I was interested in a novel machine learning method called self-validated ensemble modeling (SVEM), which promises to be uniquely useful for analysing the smaller datasets that we typically produce in industrial R&D experiments. The algorithm involves looping through hundreds of cycles of an analysis routine, which you would not want to do manually. I spent a few hours writing some code to do it and the metaphorical broken code bin was soon full. Yet it was a fun way to gain a deeper understanding of SVEM, just as you might gain a greater appreciation of the form and function of flasks and funnels by trying to make your own.

From my limited explorations it looks like SVEM is useful. But I don't think anyone should write their own code for it. You could risk using mine, but even I don't use it anymore. That's because proper software developers have since done a much better job: the most recent version of JMP Pro contains a simple interface that lets anyone analyse their data with SVEM in just a few clicks . The great thing about code is that one person can produce something once that can be endlessly re-used by any number of other people.



Focus on skills that add value

Most of the tasks that I needed to write code for in the past can now be done in this point-and-click manner and there has been an explosion in the number of commercial no-code or low-code lab automation and data software solutions in recent years. Just as with companies that mass produce glassware, software companies have been set up by people that understand the challenges and, working with the scientific community, their dedicated developers have created easy-to-use tools specifically to meet these needs. Learning how to build your own digital tools will be a waste of time for most people.

Yet digital transformation – and developing the skills needed to achieve it – remains one of the biggest challenges that organisations face today. I talk to scientists from companies big and small from all around the world and nobody has yet cracked it. One approach that I have seen work is for organisations to develop a small number of enthusiasts into in-house experts that can code bespoke solutions to streamline data workflows for their colleagues. However, this is only valuable as a later step, after the more important groundwork has been done to build the foundations for a data-driven culture.

The first step is to recognise the need for better data skills across the scientific workforce. The job of the chemist in the future will be less about making samples and more about generating data that can be turned into useful insight. The most successful organisations are already raising the baseline data literacy of all their staff and focusing on the key skills and software tools that will help their scientists to adapt to this change in the paradigm.

The chemist of the future does not need to be a coder any more than the chemist of today needs to be a glassblower. They will need to be skilled in visualisation to help them quickly explore their data and communicate insights. They will need an understanding of statistical modelling and the fundamentals of machine learning to extract maximum insight from both small and large data. And they will need to use statistical design of experiments to produce the most valuable data. JMP have created a free online training resource, Statistical Thinking for Industrial Problem Solving, that will give you an introduction to all of these topics. Find out more in

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the Chemistry WorldDesign of Experiments collection in partnership with JMP.

CChemistry World, 06 February 2023

https://chemistryworld.com

Impact of disinfectants on antibiotic resistance revealed

2023-10-11

Acinetobacter baumannii is a bacterial pathogen that can cause blood, urinary tract and lung infections such as pneumonia, particularly within hospital settings.

It's known as an 'escape pathogen' within healthcare settings – a cause of hospital infections among patients admitted for other reasons, which can be deadly for those who are critically ill.

It's also the subject of studies into antimicrobial resistance, where pathogens build resilience to agents like antibiotics that are designed to eliminate them.

A recent study published in Nature Microbiology by a research group working across four Australian universities has found A. baumannii may be developing tolerance to antibiotics through a surprise mechanism – exposure to biocides.

Biocides are essential medicines commonly used in sanitation and infection control. They include hospital and household-grade antiseptics and disinfectants containing chlorhexidine, benzalkonium and the bleaching agent sodium hypochlorite.

But at low levels, it appears that these chemicals could be inadvertently causing bacteria to develop resistance.

"We've been using them for 50-60 years, but the funny thing is we don't really know how they work," says Associate Professor Amy Cain, a microbiologist at Macquarie University who led the study.

To understand the mechanism by which biocides work, Cain and her colleagues genomically evaluated the effect 10 low-concentration biocides had on A. baumannii. Rather than bursting the bacterial cells – as was assumed they would – nearly three-quarters of those chemicals tested instead dissipated their membrane potential, without actually damaging the bacterial cell's membrane.

Australian scientists investigating the emergence of antimicrobial-resistant bacteria have found commonly used disinfectants and antiseptics may be giving dangerous pathogens a helping hand.

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In effect, they 'de-energised' the cell and its ability to exchange material

across its membrane. This loss of membrane potential diminishes the ability of antibiotics that target the interior of a cell – if the antibiotic can't get inside the bacteria, it won't find its target.

"They basically zapped the cells of energy, and this means that not only is the cell not able to function, but they can't take up antibiotics as a secondary effect.

"If there are low levels of biocide around, then the cells can't pick them up."

While this is a lab-based study, Cain and her colleagues suggest their findings have implications for the use of sanitary agents, namely that repeated use of low-concentration biocide could create conditions that impede antibiotic treatment in hospitals.

"There's no causative relationship yet – we haven't studied that – but there is an implication that by over sterilising and allowing a buildup of biocides to occur, it might have an effect on antibiotic treatment later."

The solution could be better regulation of these products.

Cain and her colleagues emphasise the importance of biocides in healthcare and households.

But some biocides are being reevaluated in light of new scientific understanding of their effects. One such chemical is triclosan. Triclosan was once a common additive to 'antibacterial' soap, but in 2016, both the European Union and US Food and Drug Administration banned its use after authorities agreed there was insufficient evidence of their effectiveness or safety in preventing the spread of illness or infection. In 2017, a group of 200 scientists and medical professionals called for greater stringency in the use of the product and other antimicrobial chemicals where evidence was lacking.

Although low-evidence biocides like triclosan are harder to come by in Australian handwash products today, this is more due to the regulatory policies of other jurisdictions like Europe and the US, says Dr Francesca Short. She's a microbiologist at Monash University who collaborated on Cain's paper. She's also investigating the potential for greater biocide regulation in Australia.

"Triclosan is currently allowed in soaps in Australia. In a lot of countries it's banned and it has very well documented links to antibiotic resistance," Short says.

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"It's not used very much [in Australia] because it's banned in so many other places and because a lot of consumers want to avoid it, so companies have stopped putting in their products.

"But you can still find it around a bit, so I think that's an example of one that we would want to get out of soap straight away."

Short has recently led a not-yet-reviewed study into the potential for biocides in commonly available supermarket and over-the-counter pharmacy products to drive antimicrobial resistance – or AMR – often containing agents like citric acid, ethanol and benzalkonium chloride in products like disinfectant wipes, toilet cleaners, sprays, hand soaps, washes and sanitisers.

She says while the Therapeutic Goods Administration is obliged to regulate some products, not all fall in the TGA's remit. Along with Cain, she's hoping to make progress in getting antimicrobial resistance considered more stringently.

"The TGA does regulate things that are claimed to prevent specific diseases, but just blanket anti-microbial activity isn't considered in that sort of claim," Short says.

"They regulate the terms 'household grade disinfectant' and 'hospital grade disinfectant' and then there's a bunch of tests you have to do to show how well your products works and claims like 'kills COVID' or 'kills Staph aureus' [a bacteria] – if you make that claim then your product's regulated by the TGA.

"But if you just say kills 99.9% of bacteria, then it's not."

"I think that [for] products that are intended to kill microbes, if people are using them for hygiene and to prevent disease, then they probably should come on to the TGA."

Cosmos, 11 October 2023

https://cosmosmagazine.com

Chemours is responsible for PFAS pollution, Dutch court rules

2023-10-06

Chemours will be held accountable for environmental damage in the Netherlands caused by releases of dangerous per- and polyfluoroalkyl

Interim decision holds DuPont spin-off liable for environmental damage caused by historical emissions from Dordrecht plant

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substances (PFAS) between 1984 and at least 1998, the Dutch district court in Rotterdam ruled in an interim decision on 27 September. This civil case

involves releases from a plant in Dordrecht.

Chemours said it is 'currently studying' the interim ruling, while stressing the importance of looking beyond this judgment. 'Irrespective of any potential future legal processes, which can often take years, we would like to find a way to take (concrete) action towards our environment sooner. We hear the concerns of residents near our location in Dordrecht and they affect us,' the company said in a statement.

'These actions will focus on mapping out an approach and on providing technical and financial support,' the company added, noting for example the potential of a fund with which the municipalities involved can finance such activities, through a joint consultation.

A final ruling is expected next year, which will include a determination about Chemours and its predecessor DuPont's culpability for PFAS pollution after 1998. 'Apart from the possibility to appeal that decision, a separate case will be needed in order to determine any damages,' the company stated.

On its website, Chemours says it takes its obligation to manage PFAS compounds in a responsible manner 'very seriously'. The company says it has committed to eliminate at least 99% of PFAS air and water emissions from its manufacturing processes by 2030. At Dordrecht, Chemours reports investing €75 million (£65 million) towards reducing these releases by more than 99% compared to 2017 baseline levels, with significant milestones expected to be achieved in 2024.

Separately, a criminal class action lawsuit against was filed against Chemours in the Netherlands on 4 September, reportedly on behalf of at least 2700 people living near the Dordrecht plant and in other municipalities. The suit apparently accuses Chemours and DuPont of knowingly discharging dangerous PFAS into the local environment since the early 1960s, and seeks a criminal investigation of Chemours as well as the possible prosecution of former executives.

Chemours said it doesn't know the contents of that criminal filing, but understands that it seeks an investigation of the company by the public prosecutor.

Meanwhile, in May the Dutch government announced that it would hold 3M responsible for contaminating the Westerschelde estuary with PFAS,

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various news outlets reported. While in Belgium, the Flemish government reached a €571 million (£494 million) agreement with 3M in July 2022, mostly to help remediate PFAS contamination in the Flanders region.

Chemistry World, 06 October 2023

https://chemistryworld.com

Getting to the Root of Tomato Toxins

2023-10-09

Such metabolites function as nutrients and chemical signals, affecting the formation of microbial communities that greatly influence plant growth.

Previous studies have found that plant-based organic toxins -- saponins, such as tomatine -- alter the microbial community around tomato roots by increasing the bacterium Sphingobium. Yet, what remained unknown was how the microbe's colonies in the tomato rhizosphere -- the soil surrounding the roots -- dealt with tomatine.

Now, a research group led by Kyoto University has revealed that Sphingobium possesses a series of enzymes that hydrolyze tomatine, detoxifying it.

"We also identified enzymes that convert the steroidal tomatidine to nontoxic, smaller compounds," says Akifumi Sugiyama of KyotoU's Research Institute for Sustainable Humanosphere.

"Our discovery of these metabolites helps us to understand how soil microorganisms cope with plant-derived toxic compounds to inhabit the rhizosphere successfully," adds Masaru Nakayasu, also at RISH.

Sugiyama's team isolated several bacteria from tomato roots and tomatine-infused soil and identified the bacterial strain RC1, which downgrades tomatine and utilizes it as a carbon source.

Sequence analyses of RC1's genes demonstrated that the expression of several genes of the glycohydrolase family increased in the presence of tomatine. The expressions of the proteins encoded by the genes of the bacterium E Coli confirmed their ability to degrade tomatine in vitro.

"We had thought the four sugars attached to tomatine degraded in some order but discovered that the four corresponding genes SpGH3-4, SpGH39-1, SpGH3-1, and SpGH3-3 jointly work to hydrolyze tomatine to tomatidine," noted Kyoko Takamatsu at KyotoU's Graduate School of Agricultural Science.

Regardless of how one says 'tomato,' they all contain tomatine, a toxin in the plant's green fruit, leaves, and roots.

Tomatoes produce the bitter-tasting compound -- a major plant-specialized metabolite secreted from the roots -- to defend against pathogens and foragers.



The authors anticipate further efforts to develop saponins other than tomatine and analyze how the saponin-degrading genes affect the interaction between plants and bacterial communities in the rhizosphere.

"Given that many plant-specialized metabolites offer human health benefits, we can engineer the bacterial genes based on their enzymatic functions to produce new bioactive compounds for human applications," concluded Sugiyama.

Technology Networks, 09 October 2023

https://technologynetworks.com

A self-wrinkling coating for impact resistance and mechanical enhancement

2023-10-12

Inspired by natural organisms' bottom-up fabrication and energy dissipation mechanisms, researchers considered four critical factors in material design (chemical composition, nano/microstructure, architecture and manufacturing techniques). They developed a self-wrinkled photocuring coating, comprising a microphase-separated structure with a gradient cross-linked architecture, as protective materials.

The self-wrinkled surface morphology induced by photo-polymerization and the intrinsic gradient architecture generated by gradient cross-linked polymer networks are critical factors for energy dissipation and impact resistance of the cured coating, providing mechanically enhanced characteristics, which was verified both theoretically and experimentally.

Compared with the highly sophisticated tools (i.e., molding, nano-/micro-imprinting, laser ablation and soft lithography) this self-wrinkled coating was fabricated through the same one-step approach as the conventional photo-curing coating, opening up new possibilities for photo-curing coatings.

Phys Org, 12 October 2023

https://phys.org

Polymer coating is widely used as a protective layer in various fields such as surface anti-corrosion, anti-penetration and anti-impact. How to enhance the mechanical properties of coatings such as impact resistance is important but challenging, under the condition of the existing materials systems and processes.

Protein Vital for Placental Health Could Be a Target for Reproductive Conditions

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The findings, they say, could lead to new treatments for reproductive conditions in the future.

The study, led by Yale School of Medicine's Reshef Tal, was published Oct. 10 in the journal JCI Insight.

A human fetus contains genetic material from both parents, which makes it partly foreign to the pregnant person's body. The immune system, therefore, needs to make adjustments that balance a tolerance for the developing fetus with protection against harmful foreign insults like viruses.

Many of these adaptations happen within the decidua — tissue that surrounds and interfaces with the placenta. Prior studies by the same research team showed that early in pregnancy, bone marrow cells, including immune cells, migrate to the uterus and the decidua. And the researchers were interested in the mechanisms that recruit these cells to the pregnant uterus.

Previous research has shown that a protein called C-X-C chemokine receptor type 4, or CXCR4, and the protein that binds to it are critical for trafficking bone marrow cells in organs and tissues around the body. CXCR4 is also expressed in higher amounts in the uterus at the beginning of pregnancy.

"Previous findings imply there is an important function for CXCR4 in pregnancy," said Tal, assistant professor of obstetrics, gynecology, and reproductive sciences at Yale School of Medicine and senior author of the study. "We wanted to understand its overall role in pregnancy maintenance and immune function in the decidua."

First, the researchers deleted the gene that codes for CXCR4 in adult female mice, effectively removing the protein from the body. Compared with normal mice, those without CXCR4 lost more fetuses during pregnancy and had smaller litter sizes. However, when CXCR4 was removed only in the uterus, there were no negative pregnancy effects.

"That finding suggested that it's not the CXCR4 expression within the uterine cells themselves, but rather it's the CXCR4 expression from outside of the uterus that plays an important role in pregnancy maintenance," said Tal.



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oxygen from the parent.

Since immune cells are recruited to the uterus from outside the organ, the researchers then looked at how CXCR4 deletion affected immune cell populations in the decidua. Early in pregnancy, the majority of immune cells in the decidua are what are known as "natural killer" cells. Around the body, these white blood cells destroy diseased cells, but in early pregnancy these natural killer cells in the decidua play a key role in the vast tissue and blood vessel remodeling required for the placenta

In mice without CXCR4, fewer natural killer cells were trafficked to the uterus and those that were clustered abnormally. These natural killer cells also expressed a particular enzyme (granzyme B) at lower levels than usual, leading to an abnormal inflammatory response in the uterus. Additionally, the mice had irregular blood vessel arrangement in the placenta and decidua, which could affect the exchange of nutrients between parent and fetus.

to properly develop and for the fetus to begin receiving nutrients and

To see if these changes were caused by immune cell dysfunction, the researchers transplanted healthy bone marrow from normal mice into mice without CXCR4.

"We found that this rescued much of the effects," said Tal.

Mice with transplanted bone marrow had fewer pregnancy losses than those without. They also had normal levels of natural killer cells, cell distribution, expression of enzymes, and blood vessel arrangement in the placenta, the researchers found.

"One of the main takeaways of the study is that you can harness the bone marrow cells' ability to home to the uterus and affect both the immune status of the decidua and the vascular remodeling of the placenta," said Tal.

This, he said, could inform new treatments for reproductive conditions like recurrent pregnancy loss and preeclampsia.

"In these conditions, there is thought to be an imbalance in the immune factors and the factors involved in blood vessel formation," said Tal. "Our findings could potentially lead to a cell therapy approach to treat those types of conditions."

Technology Networks, 11 October 2023

https://technologynetworks.com

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Gold Reinvented: Stanford Scientists Uncover Exotic Chemical State in New Material

2023-10-12

research.

For the first time, Stanford researchers have found a way to create and stabilize an extremely rare form of gold that has lost two negatively charged electrons, denoted Au2+. The material stabilizing this elusive version of the valued element is a halide perovskite—a class of crystalline materials that holds great promise for various applications including more-efficient solar cells, light sources, and electronics components.

Surprisingly, the Au2+ perovskite is also quick and simple to make using off-the-shelf ingredients at room temperature.

"It was a real surprise that we were able to synthesize a stable material containing Au2+—I didn't even believe it at first," said Hemamala Karunadasa, associate professor of chemistry at the Stanford School of Humanities and Sciences and senior author of the study published recently in Nature Chemistry. "Creating this first-of-its-kind Au2+ perovskite is exciting. The gold atoms in the perovskite bear strong similarities to the copper atoms in high-temperature superconductors, and heavy atoms with unpaired electrons, like Au2+, show cool magnetic effects not seen in lighter atoms."

Structure of the gold-halide perovskite. The elongated gold-chloride octahedra, composed of gold (Au) surrounded by six neighboring chlorine (CI) atoms, are shaded in the structure: burnt-red octahedra represent Au2+-chloride and gold octahedra represent Au3+-chloride. Turquoise spheres represent cesium (Cs) atoms, and light- green spheres represent chlorine (CI) atoms. The inset shows the shortest gold-chloride bonds. Credit Karunadasa et al. 2023.

"Halide perovskites possess really attractive properties for many everyday applications, so we've been looking to expand this family of materials," said Kurt Lindquist, the lead author of the study who conducted the research as a Stanford doctoral student and is now a postdoctoral scholar in inorganic chemistry at Princeton University. "An unprecedented Au2+ perovskite could open some intriguing new avenues."

Heavy Electrons in Gold

As an elemental metal, gold has long been valued for its relative scarcity as well as its unmatched malleability and chemical inertness—meaning

Stanford scientists have synthesized a rare form of gold, Au2+, stabilized by halide perovskite, with potential applications in electronics and energy sectors, linking their findings to Nobel laureate Linus Pauling's earlier



it can be easily shaped into jewelry and coins that do not react with chemicals in the environment and tarnish over time. An additional key reason for its value is gold's namesake color; arguably no other metal in its pure state has such a distinctively rich hue.

The fundamental physics behind gold's acclaimed appearance also explains why Au2+ is so rare, Karunadasa explained.

The root reason is relativistic effects, originally postulated in Albert Einstein's famed theory of relativity. "Einstein taught us that when objects move very fast and their velocity approaches a significant fraction of the speed of light, the objects get heavier," Karunadasa said.

This phenomenon applies to particles, too, and has profound consequences for "massive" heavy elements, such as gold, whose atomic nuclei boast a large number of protons. These particles collectively exert immense positive charge, forcing negatively charged electrons to whirl around the nucleus at breakneck speeds. As a consequence, the electrons grow heavy and tightly surround the nucleus, blunting its charge and allowing outer electrons to drift farther than in typical metals. This rearrangement of electrons and their energy levels leads to gold absorbing blue light and therefore appearing yellow to our eye.

Because of the arrangement of gold's electrons, thanks to relativity, the atom naturally occurs as Au1+ and Au3+, losing one or three electrons, respectively, and spurning Au2+. (The "2+" indicates a net positive charge from the loss of two negatively charged electrons, and the "Au" chemical symbol for gold hails from "aurum," the Latin word for gold.)

A Squeeze of Vitamin C

With just the right molecular configuration, Au2+ can endure, the Stanford researchers found. Lindquist said he "stumbled upon" the new Au2+- harboring perovskite while working on a broader project centered on magnetic semiconductors for use in electronic devices.

Lindquist mixed a salt called cesium chloride and Au3+-chloride together in water and added hydrochloric acid to the solution "with a little vitamin C thrown in," he said. In the ensuing reaction, vitamin C (an acid) donates a (negatively charged) electron to the common Au3+ forming Au2+. Intriguingly, Au2+ is stable in the solid perovskite but not in solution.

"In the lab, we can make this material using very simple ingredients in about five minutes at room temperature," said Lindquist. "We end up with

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a powder that's very dark green, nearly black, and is surprisingly heavy because of the gold it contains."

Recognizing that they may have hit new chemistry paydirt, so to speak, Lindquist performed numerous tests on the perovskite, including spectroscopy and X-ray diffraction, to investigate how it absorbs light and to characterize its crystal structure. Stanford research groups in physics and chemistry led by Young Lee, professor of applied physics and of photon science, and Edward Solomon, the Monroe E. Spaght Professor of Chemistry and professor of photon science, further contributed to studying the behavior of Au2+.

The experiments ultimately bore out the presence of Au2+ in a perovskite and, in the process, added a chapter to a century-old story of chemistry and physics involving Linus Pauling, who received the Nobel Prize in Chemistry in 1954 and the Nobel Peace Prize in 1962. Early in his career, he worked on gold perovskites containing the common forms Au1+ and Au3+. Coincidentally, Pauling also later studied the structure of vitamin C—one of the ingredients required to yield a stable perovskite containing the elusive Au2+.

"We love Linus Pauling's connection to our work," Karunadasa said. "The synthesis of this perovskite makes for a good story."

Looking ahead, Karunadasa, Lindquist, and colleagues plan to study the new material further and tweak its chemistry. The hope is that an Au2+ perovskite can be used in applications that require magnetism and conductivity as electrons hop from Au2+ to Au3+ in the perovskite.

"We're excited to explore what an Au2+ perovskite could do," Karunadasa said.

SciTechDaily, 12 October 2023

https://scitechdaily.com

Do liposomes make food supplements more effective? A chemistry expert explains common myths about these products

2023-09-28

Liposomes have been used to enhance the effectiveness of medicines since 1995. They are nano-size bubbles from a group of fatty or oily compounds called phospholipids – the building blocks of all the cells in

There has been an explosion in nutritional supplements that promise a superior product because they contain nanoparticles called liposomes. But there's a lot of misleading information and outright myths about these being shared online, so it's important to understand how liposomes work before you spend money on an expensive new food supplement.

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your body. Liposomes can fuse together to form a similar structure to human cell membranes while retaining a liquid core.

This structure gives them a unique ability to carry medicines inside their shell. While many medicines would dissolve straight away on contact with your body fluids, liposome shells can protect them until they reach the part of your body the medicine is supposed to treat.

Liposome use in the pharmaceutical industry and clinical research is regulated, meaning they are tested by independent organisations to see whether they perform as well as the manufacturers claim. There is also large body of research demonstrating how effective they are as medicine carriers.

Pharmaceutical vs food supplement liposomes

People are becoming more aware that your body is better at absorbing vitamins and other nutrients from food rather than supplements. This means food supplement companies are having to work harder to convince people their products can overcome this problem.

It may seem logical that if liposomes work well for medicines, they could help your body absorb vitamins and other supplements too. But it's not that simple. In the food supplement industry, there are a multitude of products on the market that are of poor quality or downright fake. This is due to the lack of rigorous regulation in the industry, especially for advanced formulations like liposomes.

Since their discovery in 1966, the structure of liposomes has been developed for several applications in the medical field, including prolonged circulation (making the medicine stay in your system longer), targeted delivery, and controlled release. In 1995, Doxil(R) was the first liposomal drug licensed for cancer treatment. It is a type of chemotherapy which uses liposomes to give the drug more time to reach tumour tissue, where the drug is slowly released.

But researchers achieved this using complicated processes that are expensive and demand a high level of skill. For example, some medical liposomes use cholesterol in the outer shell to keep it intact for longer.

In contrast, the liposomes used in food supplements are often the most basic, delicate type. The more delicate the liposome, the faster it breaks down

Do liposomes enhance oral absorption?

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There are conflicting reports about whether liposomes enhance gastrointestinal absorption.

Food supplement liposomes may enhance absorption by improving the ability of the nutrients they contain to fuse with other substances in your food. However, there is limited evidence that even advanced types of liposome pass through the stomach and small intestine membrane into the bloodstream.

And even if the liposomes can reach the blood intact, they will then be attacked by your immune system as a foreign substance. Medicinal liposomes are better equipped to withstand this kind of attack.

Conventional liposomes are easily destroyed in the stomach and small intestine. This means claims that such liposomes protect nutrients from stomach acid are false. The same goes for claims that conventional liposomes are absorbed into your bloodstream and remain intact. Similarly, claims that food supplement liposomes carry nutrients through the gut, into circulation, and then travel to organs are a work of fiction, as a review of 50 years of liposome research showed.

Can liposomes be used with any type of nutrient?

The simple answer is no. There are many nutrients that liposomes struggle to encapsulate for different reasons.

Firstly, some nutrients are made from molecules too big to fit inside a liposome. It would be like trying to fit a full trolley of food inside one small plastic bag. Even in pharmaceutical research, where more advanced techniques are used, some drug molecules are difficult to fit inside liposomes.

Furthermore, liposomes are not an impervious plastic bag, but more akin to a cotton bag through which water can pass. This sometimes leads to content leakage. Water-soluble materials such as vitamin C or vitamin B are thus even trickier to encapsulate than fat-soluble ones such as vitamin D, curcumin or resveratrol.

In pharmaceutics, the maximum loading is 10% drug molecules to lipid molecules (fatty compounds that perform a variety of functions in your body). This means if you take a dose, only 10% of it will consist of the drug molecules encapsulated in liposomes. In the case of food supplements, the ratio is higher but claims of 100% encapsulation efficiency are simply not possible.



And unfortunately, it is not possible to tell whether a product contains liposomes just by looking at it. Liposomal formulations are watery rather than creamy or gel-like. Manufacturers add thickening agents and other additives to make their products look more appealing – so neither colour nor thickness can tell you whether a product contains high-quality liposomes, as some companies may claim.

If a company says its products contain liposomes, always check its website for evidence such as electron microscope imaging in production. The sizes of liposomes vary, but it is impossible to see them without a microscope.

While it might be possible to see larger liposomes using a quality light microscope, the smaller and more effective liposomes are measured in nanometres. They can only be seen with more sophisticated, electron-scanning microscopy.

Ultimately, until there is better regulation of nutritional supplements, it is difficult to verify these businesses' claims about how they make their products, and what is and isn't in them.

The Conversion, 28 September 2023

https://theconversion.com

Breakthrough Technology Selectively Removes Aging Cells

2023-10-04

Aging cells, known as senescent cells, contribute to various inflammatory conditions and age-related ailments as humans age. To address this issue, the research team focused on developing a technology that could precisely target and eliminate aging cells, while sparing normal healthy cells.

In their study, the team designed organic molecules that selectively target receptors overexpressed in the membranes of aging cells. By leveraging the higher levels of reactive oxygen species (ROS) found in aging cells, these molecules promote the formation of disulfide bonds and create oligomers that bind together.

Through self-assembly of these oligomers, the researchers successfully created artificial proteins with a stable α -helix secondary structure. These protein-like nanoassemblies exhibited strong binding affinity to the mitochondrial membranes of aging cells, leading to membrane disruption and subsequent cell self-destruction.

A research team, led by Professor Ja **Hyoung Ryu from** the Department of **Chemistry at UNIST,** in collaboration with **Professor Hyewon Chung from Konkuk University**, has achieved a significant breakthrough in the treatment of age-related diseases. Their cutting-edge technology offers a promising new approach by selectively removing aging cells, without harming normal healthy cells. This groundbreaking development is poised to redefine the future of healthcare and usher in a new era of targeted therapeutic interventions.

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"The selective removal of aging cells by targeting the mitochondria and inducing dysfunction has been successfully demonstrated in our experiments," stated Professor Ryu. "This approach represents a new paradigm for treating age-related diseases."

This innovative technology offers several advantages, including minimal toxicity concerns and a wide therapeutic window by specifically targeting organelles within cells. It opens up exciting possibilities for designing preclinical and clinical trials in the future.

Technology Networks, 4 October 2023

https://technoloynetworks.com



Mutation studies reveal how Antarctic octopus arms itself with cool enzyme

2023-10-11

Researchers in the US began by investigating the workings of a crucial Na+/K+ ion pump from an octopus that had been collected below the ice in McMurdo Station, Antarctica. This Na+/K+ ion pump, powered by ATP, pushes three sodium ions out for every two potassium ions in, generating the electrochemical gradient that is critical to allow neurons to fire. In neurons, the activity of this protein uses around three-quarters of a cell's total energy output, notes Ilya Levental, a molecular physiologist at the University of Virginia.

'As we lowered the temperature, the ATPase from the Antarctica octopus kept working way faster than the temperate octopus [one], which pretty much stopped once we reached 8°C,' recalls Miguel Holmgren at the National Institute of Neurological Disorders and Stroke in Bethesda, Maryland. At 10°C, the Antarctic octopus pump is around four times more active than the temperate version, previous experiments have shown.

To reveal why, Holmgren and his colleagues injected the RNA message that codes for the Antarctic and temperate octopus enzymes into the unfertilised eggs of a Xenopus frog. They tweaked the amino acid sequences to make chimeras more or less like the Antarctic enzymes.

The enzyme in the Antarctic cephalopod had previously been found to differ from the warm water one in 35 out of 1028 amino acids. Just 12 mutations allowed the temperate enzyme to replicate the cold tolerance of the Antarctic enzyme. Surprisingly, a single amino acid change allowed substantially higher activity in the face of extreme cold – switching a valine for a leucine at the interface of the protein and the lipid.

This single amino acid switch makes the opening of the ion pump more hydrophobic, so that it slips more easily into the cell's membrane. 'The amino acid made the protein greasier, says Holmgren. The more greasy, the lower the energy required to move from one conformation to another and the faster the pump.'

Enzymes adapt to the cold by becoming 'floppier', so they need less energy to undergo conformational changes, something that is necessary when there is less thermal energy around, says Levental. 'Membrane proteins have an added challenge of being in a lipid environment that is itself affected by cold, he adds.

A handful of amino acid mutations in an enzyme from an Antarctic octopus equips it with remarkable cold tolerance. The discovery came from comparing enzymes from a cold-water and a temperate-water species. Insight into the cold-adapted enzyme might have relevance for cryogenic preservation or organ transplantation.

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The results 'suggest that non-specific, physical interactions between proteins and lipids – rather than protein folding – are very important for cold adaption', says Levental. 'This is cool because it shows how important the subtle interactions between transmembrane domains and their solvating lipids can be.'

Enzyme cold adaptation is a much more interesting problem than heat adaptation, says Johan Agvist, a biochemist at Uppsala University, Sweden and chair of the Nobel committee for chemistry. This latest research is impressive, he adds, and similar to his report on a globular enzyme, which found that the protein surface facing the solvent is mostly responsible for cold adaptation. He also notes that the engineered pump's activation enthalpy has been reduced, just as in normal cold-adapted enzymes.

Though speculative, cold tolerance in enzymes may one day be important for cryogenic medicine or preservation or for organ transplantation, suggests Levental. It appears to me that maybe the principles for adaptation of membrane-bound enzymes are not very different from regular enzymes.'

Chemistry World, 11 October 2023

https://chemistryworld.com

Genetically engineered chickens could help slow spread of bird flu

2023-10-10

Avian influenza, or bird flu, is a tricky disease to control. It's adaptable and highly transmissible, and can be spread long distances thanks to the freedom of movement migratory birds enjoy. Large-scale farming of chickens for meat and eggs accelerates the spread and mutation rate of the virus, and once it's in a population farmers and authorities often have to resort to culling birds by the millions to try to curb it.

For the new study, scientists in the UK investigated how practical it might be to genetically engineer chickens to be more resistant to bird flu. Previous studies have shown that a protein called ANP32A is usually the target for the virus to replicate, so the team altered the gene that produces this protein.

The gene-edited chickens were then exposed to a normal dose of the H9N2-UDL strain of the virus through close contact with infected birds. And sure enough, 90% of the engineered birds resisted infection, and

The world may be quickly forgetting about COVID-19, but there are signs the next pandemic is already cooking up – bird flu. Scientists have now demonstrated that genetically engineering chickens can reduce their chances of catching and spreading the disease, but it's not foolproof.



didn't spread it to other chickens. No adverse effects to their health or growth was detected.

Next, the team tested a much higher dose of the virus – 1,000 times that of natural exposure. In this case, 50% of the chickens were infected, although the levels of the virus in the inoculated birds remained much lower than in non-edited chickens. Even against the higher doses, the gene edits reduced the onward spread of the virus, infecting just one of four non-edited chickens and no gene-edited birds that shared an enclosure with the infected, edited chickens.

Editing a single gene may not be enough, however. Testament to the virus' frustrating ability to evolve quickly, it was found that it could bypass the deleted ANP32A gene and still replicate using related proteins ANP32B and ANP32E. Follow-up tests in lab-grown chicken cells showed that knocking out all three genes successfully blocked growth of the virus, but unfortunately this combo is expected to affect the health of chickens.

While this gene-editing approach may have some benefits – even if they're limited to safeguarding the world's supply of chicken nuggets – other scientists say it isn't enough to curb bird flu significantly.

"If chickens could be engineered to be resistant to avian influenza viruses, that may reduce the risk of the emergence of a human pandemic virus from avian influenza," said Professor Raina MacIntyre, an expert in influenza and emerging infectious diseases at the University of NSW. "However, avian influenza spreads globally not just through poultry trading, but also through wild waterfowl such as ducks and geese. These birds can spread avian influenza as they migrate across flyways between countries and continents, independent of farmed poultry. So, engineering farmed chickens alone is not enough.

"The other main concern is influenza A viruses are highly mutable and subject to continual antigenic drift. This means the virus itself will likely evolve to overcome engineered traits in the birds."

The researchers say that further work will continue to help shore up the chicken population against bird flu.

The research was published in the journal Nature Communications.

New Atlas, 10 October 2023

https://newatlas.com

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Some Plants May Worsen Air Pollution in a Warming World

2023-10-06

OCT. 13, 2023

Trees including oak and poplar will emit more isoprene — a compound that worsens air pollution — as global temperatures rise, according to new MSU research.

It's a simple question that sounds a little like a modest proposal.

"Should we cut down all the oak trees?" asked Tom Sharkey, a University Distinguished Professor in the Plant Resilience Institute at Michigan State University.

Sharkey also works at the MSU-Department of Energy Plant Research Laboratory and in the Department of Biochemistry and Molecular Biology.

To be clear, Sharkey wasn't sincerely suggesting that we should cut down all the oaks. Still, his question was an earnest one, prompted by his team's latest research, which was published in the scientific journal Proceedings of the National Academy of Sciences.

The team discovered that, on a warming planet, plants like oaks and poplars will emit more of a compound that exacerbates poor air quality, contributing to problematic particulate matter and low-atmosphere ozone.

The rub is that the same compound, called isoprene, can also improve the quality of clean air while making plants more resistant to stressors including insects and high temperatures.

"Do we want plants to make more isoprene so they're more resilient, or do we want them making less so it's not making air pollution worse? What's the right balance?" Sharkey asked. "Those are really the fundamental questions driving this work. The more we understand, the more effectively we can answer them."

Spotlight on Isoprene

Sharkey has been studying isoprene and how plants produce it since the 1970s, when he was a doctoral student at Michigan State.

Isoprene from plants is the second-highest emitted hydrocarbon on Earth, only behind methane emissions from human activity. Yet most people have never heard of it, Sharkey said.

Trees including oak and poplar will emit more isoprene – a compound that worsens air pollution – as global temperatures rise.



"It's been behind the scenes for a long time, but it's incredibly important,"

It gained a little notoriety in the 1980s, when then-president Ronald Reagan falsely claimed trees were producing more air pollution than automobiles. Yet there was a kernel of truth in that assertion.

Sharkey said.

Isoprene interacts with nitrogen oxide compounds found in air pollution produced by coal-fired power plants and internal combustion engines in vehicles. These reactions create ozone, aerosols and other byproducts that are unhealthy for both humans and plants.

"There's this interesting phenomenon where you have air moving across a city landscape, picking up nitrogen oxides, then moving over a forest to give you this toxic brew," Sharkey said. "The air quality downwind of a city is often worse than the air quality in the city itself."

Now, with support from the National Science Foundation, Sharkey and his team are working to better understand the biomolecular processes plants use to make isoprene. The researchers are particularly interested in how those processes are affected by the environment, especially in the face of climate change.

Prior to the team's new publication, researchers understood that certain plants produce isoprene as they carry out photosynthesis. They also knew the changes that the planet is facing were having competing effects on isoprene production.

That is, increasing carbon dioxide in the atmosphere drives the rate down, while increasing temperatures accelerate the rate. One of the questions behind the MSU team's new publication was essentially which one of these effects will win out.

"We were looking for a regulation point in the isoprene's biosynthesis pathway under high carbon dioxide," said Abira Sahu, the lead author of the new report and a postdoctoral research associate in Sharkey's research group.

"Scientists have been trying to find this for a long time," Sahu said. "And, finally, we have the answer."

"For the biologists out there, the crux of the paper is that we identified the specific reaction slowed by carbon dioxide, CO2," Sharkey said.

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"With that, we can say the temperature effect trumps the CO2 effect," he said. "By the time you're at 95 degrees Fahrenheit — 35 degrees Celsius — there's basically no CO2 suppression. Isoprene is pouring out like crazy."

In their experiments, which used poplar plants, the team also found that when a leaf experienced warming of 10 degrees Celsius, its isoprene emission increased more than tenfold, Sahu said.

"Working with Tom, you realize plants really do emit a lot of isoprene," said Mohammad Mostofa, an assistant professor who works in Sharkey's lab and was another author of the new report.

The discovery will help researchers better anticipate how much isoprene plants will emit in the future and better prepare for the impacts of that. But the researchers also hope it can help inform the choices people and communities make in the meantime.

"We could be doing a better job," Mostofa said.

At a place like MSU, which is home to more than 20,000 trees, that could mean planting fewer oaks in the future to limit isoprene emissions.

As for what we do about the trees already emitting isoprene, Sharkey does have an idea that doesn't involve cutting them down.

"My suggestion is that we should do a better job controlling nitrogen oxide pollution," Sharkey said.

Sarathi Weraduwage, a former postdoctoral researcher in Sharkey's lab who is now an assistant professor at Bishop's University in Quebec, also contributed to the research.

Reference: Sahu A, Mostofa MG, Weraduwage SM, Sharkey TD. Hydroxymethylbutenyl diphosphate accumulation reveals MEP pathway regulation for high CO2-induced suppression of isoprene emission. PNAS. 2023;120(41):e2309536120. doi: 10.1073/pnas.2309536120

Technology networks, 06 October 2023

https://technologynetworks.com/a>

Researchers have combined two microscopic imaging techniques in one microscope, providing scientists with a high-resolution method of tracking single molecules in a cellular context. The development opens the door to improving our ability to visualize, in minute detail, what's happening inside cells.



New two-in-one microscope gives a detailed glimpse

2023-10-10

inside cells

These days, scientists have the means of peering inside cells using incredibly powerful microscopes. It's important that they're able to do this to understand how specific biomolecules act and react. However, these tools have some drawbacks.

Take, for example, super-resolution fluorescence microscopy (SRM). It's great for tracking single molecules, like proteins, in a cell but doesn't show scientists what's happening nearby. And, while cryogenic electron tomography (cryo-ET) yields high-resolution images of cells, it can't pinpoint what individual molecules are up to.

So, researchers at the US Department of Energy's Stanford Linear Accelerator Center (SLAC) National Accelerator Laboratory set about combining the two imaging techniques into one microscope.

"The goal is to keep the best of both worlds," said Peter Dahlberg, lead author of the study. "You're retaining the molecular specificity of fluorescence microscopy, so you know who's who, and then you can put it in the context of these high-resolution structures from cryo-ET."

Fluorescence microscopy involves tagging an individual molecule with a smaller molecule that glows when a light is shone on it. The molecule can then be tracked under an ordinary – albeit very high-resolution – optical microscope. Cryo-ET uses electron microscopes to study flash-frozen samples, like cells.

Combining the two techniques immediately raised problems the researchers needed to overcome. The first was that cells containing fluorescently labeled molecules had to be dropped onto a cryo-ET grid only 3 mm in diameter, then flash-frozen quickly enough that the water on the grid turned to glass (vitrifies). Once frozen, the cell has to stay frozen. The second problem is the size of frozen cells – they are thousands of nanometers thick – but the electrons used in cryo-CT can't penetrate deeper than 200 nanometers.

So, the researchers developed a device called a focused ion beam milling system with an attached scanning electron microscope, or a FIB-SEM. The focused ion beam cuts away cellular material, leaving a very thin slice of frozen cell that cryo-ET can penetrate. Then, the scanning electron

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microscope shoots electrons at the sample to produce high-resolution images.

There was just one problem with the prototype FIB-SEM: it didn't have an optical microscope attached, which means that the cryo-ET grid had to be moved to perform fluorescence microscopy. Luckily, there was a simple fix.

"Essentially, we just ripped apart this \$1.5-million sophisticated instrument to install this integrated light microscope, and now we have a much, much better system," Dahlberg said.

Testing the FIB-SEM in 2020, tracking proteins within bacterial cells, the researchers found it worked but realized the material the cryo-ET grid was made from was absorbing light and ruining the frozen samples. So, they made some tweaks, engineering better grids and making a better stage for the light microscope.

Now, the researchers are engineering different kinds of fluorescent labels – biosensors – to work under cryogenic conditions. The biosensors are fluorescent molecules that change their emission or excitation properties depending on the local environment, glowing one color in one environment and a different color in another.

"They can be tuned to be sensitive to pH, calcium – you name it," said Dahlberg. "There are hundreds of environmental variables they can be tuned to. So, on top of the specific location and high-resolution structural information, you can also know was my cell healthy or sick? About to undergo cell division? At a high ATP concentration? It provides all this extra content."

The researchers will continue to tinker with the FIB-SEM until it's optimized and reaches its full potential.

New Atlas, 10 October 2023

https://newatlas.com

Millions carry a gene mutation scientists just linked to inflammation

2023-10-05

A team at WEHI in Melbourne discovered that 2-3% of the population have a gene mutation that could provide both 'explosive' cell death called necroptosis, and an increase in inflammation. While 2-3% of the

a gene mutation in a small but significant portion of the population, and using cells and mice models have found the mutation increases inflammation. If this is translated to humans it may raise the risk of inflammatory diseases like inflammatory bowel disease.



population doesn't sound high, around the world this could mean millions

"Programmed cell death is something that happens all the time, all over the body, millions and millions of cells are being cleaved by the body, and that's really important," says WEHI's Dr Joanne Hildebrand, one of the researchers from the new study.

of people have the mutation.

"We found that between 2-3% of people in the world carry a small change in one of their genes that is really important for programmed cell death. We think that particular change makes these people a little bit better at performing a form of programmed cell death called necroptosis."

The biochemists had been studying a particular gene called MLKL, which is an important protein involved in necroptosis. While they don't normally look at population genetics, they started looking into it after discovering a number of people with inflammatory diseases who had a particular mutation called p.Ser132Pro in the protein.

"I had a look at that mutation [inside a gene database] and went 'oh my God, there's so many people out there carrying this variant, I reckon it might be worth having a look to see if it does anything," said Hildebrand.

"And so, we made that same change in the mouse version of the gene."

When the researchers looked at the gene in both human and mouse cells they found that the gene mutation caused more of the protein to accumulate, allowing a more 'explosive' necroptosis. But they also found that it increased inflammatory properties.

In mice models, the mutation made the mice less able to clear a salmonella infection, suggesting that although it causes more necroptosis, this likely not a beneficial mutation.

"We want to know, what's the point of having a gene change like this? Is it a good thing? Is that a bad thing?" says Hilderbrand.

"Because programmed cell death is so important to the immune system, our hypothesis is that somewhere in human history having this particular gene change made carriers more likely to survive in the event of a certain infection, whether it's a viral infection or a bacterial infection."

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Researchers have released a paper published in Nature Communications investigating the potential link.

Cosmos, 05 October 2023

https://cosmosmagazine.com

Researchers develop new class of catalysts for green production of fine chemicals and pharmaceuticals

2023-10-11

OCT. 13, 2023

Fine chemical and pharmaceutical manufacturing are major sources of air pollution, with recent studies showing the carbon footprint of the pharmaceutical industry to be heavier than the automotive industry. Beyond greenhouse gas emissions, the pharmaceutical industry is also responsible for other serious environmental impacts, such as water pollution from wastewater released by manufacturers.

"Developing alternative catalytic systems capable of achieving atomic-level precision while ensuring recoverability is at the forefront of our mission to revolutionize sustainable manufacturing processes for fine chemicals and pharmaceuticals. This ground-breaking achievement is the outcome of a close collaboration between several institutions," said Associate Professor Lu Jiong from the Department of Chemistry under the NUS Faculty of Science, who led the team of NUS researchers.

The study was a collaboration involving Associate Professor Koh Ming Joo and Assistant Professor Zhu Ye from the Department of Chemistry under the NUS Faculty of Science, Professor Li Jun from Tsinghua University in China, Professor Javier Pérez-Ramírez from ETH Zurich in Switzerland and Dr. Xi Shibo from the Agency for Science, Technology and Research (A*STAR) in Singapore. The research was published in the journal Nature on 20 September 2023.

Developing a new class of catalyst

The synthesis of organic compounds requires a series of steps known as transition metal-catalyzed coupling reactions. These chemical reactions are indispensable for forming essential chemical bonds during the synthesis of a chemical compound. However, catalysts that are currently used in these reactions pose a number of challenges, such as high production cost, difficulty in catalyst separation for recovery and reuse, and metal contamination which is harmful to the environment. The

A research team has developed a new class of catalysts—known as heterogeneous geminal atom catalysts (GACs)—that promotes greener and more sustainable manufacturing processes for fine chemicals and pharmaceuticals.



structural architecture of current catalysts also limits their capacity to carry out complex reactions.

NUS researchers, together with their international collaborators, developed a new class of GACs to circumvent these challenges and boost the potential for more sustainable and environmentally friendly pharmaceutical manufacturing processes.

One key feature of this new class of catalyst is the presence of two metal cores made up of copper ions that allows for more efficient and selective reactions. The research team used a material called polymeric carbon nitride (PCN) to act as a supporting structure to hold the two copper ions for them to work together in the chemical reactions. The researchers tinkered with the structure to discover that approximately 0.4 nanometers was the perfect distance between these two copper ions for them to function as one unit to carry out important chemical reactions.

The novel catalyst takes on a unique heptazine chain structure that allows it to be dynamic and adaptable during chemical reactions for the two copper ions to efficiently bring two reactants together for a chemical bond to form; such a chemical reaction is known as cross-coupling. This structure also reduces the minimum amount of energy needed for a chemical reaction to occur.

The research team then tested the newly developed catalyst in some chemical reactions involved in creating commonly used drugs and chemical compounds to demonstrate its efficiency compared to conventional catalysts, and researchers also quantified the environmental benefits of this new type of GACs.

Novel GACs for greener chemical processes

To showcase the versatility of the newly developed GACs, the researchers assessed its performance in various chemical reactions, such as the formation of multifunctional heterocyclic compounds that are commonly used in the production of pharmaceuticals.

The team also reported that the new catalyst can improve the yield of the final product. For example, using the novel GACs, more bromide substrates were readily available to successfully improve the yield of dutasteride, which is used primarily to treat prostate disease, from 53% to 62%, compared to using conventional metal catalysts.

The researchers put the catalyst through nine consecutive cycles of chemical reactions, and discovered that it could remain stable with no

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detectable loss of copper ions from the original structure. This means that the amount of waste and risk of metal contamination can be significantly reduced.

In addition, the new GACs can be readily recovered and reused, underscoring its potential in boosting sustainability in the chemical and pharmaceutical industries.

The researchers also analyzed the environmental benefits of using the novel catalyst in chemical reactions and found that it achieves a carbon footprint that is 10 times lower than using conventional catalysts.

By outperforming conventional catalysts through increased yield, higher efficiency and improved environmental impact in cross-coupling reactions, this new class of GACs are an attractive option for adoption in the fine chemical and pharmaceutical industries.

"Our goal in the near future is to create a library of GACs by carefully adjusting the specific types and combinations of geminal metal centers. This can potentially transform the conventional methods of chemical production. It could signify the dawn of a new era where GACs play a pivotal role in achieving greener and more environmentally friendly chemical and pharmaceutical manufacturing," added Assoc Prof Lu.

Phys Org, 11 October 2023

https://phys.org

Why the making stuff mindset doesn't make sense 2023-10-11

I expect that there are plenty of chemists right now that have barely begun this journey. To be successful in the digital future of chemistry, scientists will need guidance and encouragement to make that change. We might even be able to avoid the making-stuff mindset taking hold in the first place.

From preps to plans

At school and university, my only experience of experiments was lab practicals. These were useful in demonstrating the synthetic routes that we were learning about and for building practical skills, but success here was often defined as a heap of large, colourless crystals. That left me thinking that experiments were about confirming our understanding of chemical mechanisms.

When I started as a development chemist in industry, a good day for me was making some stuff that was better than the stuff I had made the day before. That was my idea of success. With time, however, I realised that the product of my experiments wasn't really the stuff in the flasks, it was the stuff I was learning: the knowledge needed to consistently manufacture products that meet the demands of our customers. It was an epiphany. My job was not about making things, it was to generate understanding.



This notion was challenged immediately in my first job, as a process chemist making toner for laser printing. The system was just too complex and messy to be understood from theory alone - curly arrows were no use! Instead I spent my days painstakingly carrying out 'preps' to figure out how to combine latex, pigment dispersion and other ingredients to produce uniformly sized toner particles. With each prep, I would tweak the recipe. I might swap out a raw material, modify concentrations and proportions, or change the temperature of one of the hold phases. There was always a rationale, and I was happy that I was following the scientific method (form a hypothesis, make a prediction, test the prediction), but there was little in the way of strategy. When I arrived at something that worked, I didn't really know how I had got there. I became accustomed to the unpredictability of this approach, but I never got comfortable with it.

Mind over matter

Then I heard a seminar by statistics professor Dick de Veaux that introduced me to a new way of thinking: the data gathered from observations accumulated over many runs of an industrial process can be 'mined' for insights about the behaviours driving the system and to build a model of how the inputs will affect the outcomes. In short, rather than taking one step at a time hoping to end up at the best recipe, I could use the data holistically to make a map that shows me where to find the best recipe.

At least that was the theory. In practice, my own datasets were not very useful. Each prep took significant time and resources, so twenty rows of data was a lot for one project, and that is nobody's idea of big data. There was little or no common ground between one project and the next, so it was not worth the effort of pulling together historical data. And when I looked at the data, many of the input variables had barely been varied at all. I needed a new mindset to go with the new approach.

I needed to plan each project to deliver the data that would help me meet the development objectives. I needed to choose the inputs to vary and the outputs to measure, and how to systematically vary the inputs to optimise what I could learn from each run. Thankfully there was already a methodology for this: Statistical Design and Analysis of Experiments or DOE.

With these tools and my new outlook, my projects became more efficient and predictable, and my colleagues started to pay attention. We had some great successes, such as doubling the productivity of a bottleneck manufacturing step without needing expensive new plant infrastructure.

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Helping my colleagues with DOE became my full-time passion and professional focus.

I have since learned that many scientists and engineers have gone through similar journeys of realisation. In a recent webinar with Chemistry World, Pilar Gómez Jiménez, a principal scientist at Johnson Matthey discussed how introducing this smarter approach to experimentation helped deliver a 50% reduction in R&D costs for the business. 'Every chemical problem or every challenge that my colleagues present to me, I see it as a table with columns and rows. That is a total change in mindset...' she explained.

Like many others, Gómez Jiménez and I wish we had learned these ideas earlier in our careers. The graduate training in DOE at the Centre for Rapid Online Analysis of Reactions (Roar) at Imperial College is a rare example of bringing these ideas to students before they join industry. But why not have simple DOE exercises for undergraduates or even in high school science classes?

It's never too early nor too late to learn these skills, and you can start right now. Sign up for our online workshop, Your guide to solving complex problems by mastering Design of Experiments and begin the journey. Stop making stuff and you'll start making sense.

Chemistry World, 11 October 2023

https://chemistryworld.com

Ozone hole over Antarctica among largest on record

2023-10-1

The 'ozone depleting area' reached 26 million square kilometres on 16 September 2023, an area three times the size of Brazil, according to the European Space Agency.

European Space Agency satellites have been measuring global ozone data for almost three decades. The recent measurements were taken by the Copernicus Sentinel 5P satellite, launched in 2017 as part of the agency's environmental monitoring mission.

While the news appears bleak, the reasons for the large size of the hole are yet to be established.

The ozone hole is known to fluctuate depending on the strength of winds in the Antarctic region, and generally reaches its maximum size between mid-September and mid-October.

The hole in the Ozone layer above Antarctica is currently one of the biggest on record according to European satellite measurements.

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Ozone levels usually return to normal by the end of December, the

One possible reason for the larger-than-usual hole this year could be the result of the Hunga Tonga-Hunga Ha'apai volcano eruption in Tonga in January 2022, however the agency says further research is needed.

Senior scientist Antje Inness from the Copernicus Atmosphere Monitoring Service says in a statement: "Our operational ozone monitoring and forecasting service shows that the 2023 ozone hole got off to an early start and has grown rapidly since mid-August".

The phase out of ozone-depleting substances under the 1987 Montreal Protocol has led scientists to predict the eventual recovery of the ozone layer.

Cosmos, 10 October 2023

https://cosmosmagazine.com

European Space Agency says.

Scientists pry a secret from the 'Mona Lisa' about how Leonardo painted the masterpiece

2023-10-11

Using X-rays to peer into the chemical structure of a tiny speck of the celebrated work of art, scientists have gained new insight into the techniques that Leonardo da Vinci used to paint his groundbreaking portrait of the woman with the exquisitely enigmatic smile.

The research, published Wednesday in the Journal of the American Chemical Society, suggests that the famously curious, learned and inventive Italian Renaissance master may have been in a particularly experimental mood when he set to work on the "Mona Lisa" early in the 16th century.

The oil-paint recipe that Leonardo used as his base layer to prepare the panel of poplar wood appears to have been different for the "Mona Lisa," with its own distinctive chemical signature, the team of scientists and art historians in France and Britain discovered.

"He was someone who loved to experiment, and each of his paintings is completely different technically," said Victor Gonzalez, the study's lead author and a chemist at France's top research body, the CNRS. Gonzalez has studied the chemical compositions of dozens of works by Leonardo, Rembrandt and other artists.

The "Mona Lisa" has given up another secret.

"In this case, it's interesting to see that indeed there is a specific technique for the ground layer of 'Mona Lisa," he said in an interview with The

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Associated Press.

Specifically, the researchers found a rare compound, plumbonacrite, in Leonardo's first layer of paint. The discovery, Gonzalez said, confirmed for the first time what art historians had previously only hypothesized: that Leonardo most likely used lead oxide powder to thicken and help dry his paint as he began working on the portrait that now stares out from behind protective glass in the Louvre Museum in Paris.

Carmen Bambach, a specialist in Italian art and curator at New York's Metropolitan Museum of Art, who was not involved in the study, called the research "very exciting" and said any scientifically proven new insights into Leonardo's painting techniques are "extremely important news for the art world and our larger global society."

Finding plumbonacrite in the "Mona Lisa" attests "to Leonardo's spirit of passionate and constant experimentation as a painter—it is what renders him timeless and modern," Bambach said by email.

The paint fragment from the base layer of the "Mona Lisa" that was analyzed was barely visible to the naked eye, no larger than the diameter of a human hair, and came from the top right-hand edge of the painting.

The scientists peered into its atomic structure using X-rays in a synchrotron, a large machine that accelerates particles to almost the speed of light. That allowed them to unravel the speck's chemical makeup. Plumbonacrite is a byproduct of lead oxide, allowing the researchers to say with more certainty that Leonardo likely used the powder in his paint recipe.

"Plumbonacrite is really a fingerprint of his recipe," Gonzalez said. "It's the first time we can actually chemically confirm it."

After Leonardo, Dutch master Rembrandt may have used a similar recipe when he was painting in the 17th century; Gonzalez and other researchers have previously found plumbonacrite in his work, too.

"It tells us also that those recipes were passed on for centuries," Gonzalez said. "It was a very good recipe."

Leonardo is thought to have dissolved lead oxide powder, which has an orange color, in linseed or walnut oil by heating the mixture to make a thicker, faster-drying paste.

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But the "Mona Lisa"—said by the Louvre to be a portrait of Lisa Gherardini, the wife of a Florentine silk merchant—and other works by Leonardo still have other secrets to tell.

"There are plenty, plenty more things to discover, for sure. We are barely scratching the surface," Gonzalez said. "What we are saying is just a little brick more in the knowledge."

Phys Org, 11 October 2023

said. "It flows more like honey."

https://phys.org

Titanium oxide material can remove toxic dyes from wastewater

2023-10-10

A study lead Michel Barsoum, Ph.D., Distinguished University professor in the College of Engineering, and his team, including researchers from Drexel's College of Arts and Sciences, found that a one-dimensional, lepidocrocite structured titanium oxide photocatalyst material has the ability to break down two common dye pollutants -- rhodamine 6G and crystal violet -- under the visible light spectrum. The material also reduced those dye concentrations in the water by 90% and 64%, respectively, in just 30 minutes, when the starting catalyst to dye mass ratio was 1 to 1.

"This is an exciting finding because it helps to address a problem that has been a real challenge for the water treatment process," Barsoum said. "We anticipate that integrating our titanium-oxide photocatalyst into the current processes could improve its effectiveness in removing these chemicals, as well as reducing the amount of energy required to do so."

The process starts with adsorption, where the dye adheres to the surface of the nanofilament, and once illuminated undergoes photocatalysis. The dye sensitizes the nanofilaments to visible light. This process accelerates degradation, allowing the dye to break apart into harmless byproducts such as carbon dioxide and water.

The study, recently published in the journal Matter, found that the key to the dye degradation and self-sensitization process was the ability of the material to generate electron holes and something called "ROS" -- hydroxyl, superoxide and singlet oxygen, radicals, as well as electron "holes."

Discharged in large quantities by textile, cosmetic, ink, paper and other manufacturers, dyes carry high-toxicity and can bring potential carcinogens to wastewater. It's a major concern for wastewater treatment -- but researchers in **Drexel University's College of Engineer**ing may have found a solution, using a tiny nanofilament.

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The two dye targets are commonly appearing dye driven effluents in wastewater. Effluent, which literally means something that flows out, is different than sewage found in wastewater. Solid waste can be filtered, removed before the water is purified. Effluent is suspended in the water, making it hard to separate and remove.

Rhodamine 6G is a xanthene-derived dye primarily used in wood processing, paper dyeing, pen ink and cosmetics. Crystal violet, a triphenylmethane dye, is used to dye ink and textiles. These dyes are water soluble and any excess is discharged as effluent.

Wastewater is a major environmental concern worldwide and its existence has long-term impacts on health of humans, aquatic plants and animals. Households and industry generate nearly 380 billion cubic tons of wastewater globally each year. Only 24% of this is treated sufficiently due to challenges in treatment, including high energy consumption, the existence of residual chemicals, treatment center staffing and the insufficient processing of complex and persistent contaminants, including dyes.

The most common wastewater treatment methods, such as sedimentation, biological oxidation and chemical-physical treatment, are ineffective at removing dyes, according to the researchers, due to the dyes' complex molecular structure and water-soluble nature.

Adsorption with clay materials, activated carbon, iron oxide and natural materials such as coffee grounds, has also been used before and exhibit high cationic dye uptake, exchanging ions or forming bonds. However, these materials simply allow separation of the dye from the water -- the dye still exists and is simply attached to the adsorbent materials within the wastewater.

Photocatalysts, long thought to be the key to removing dyes from water, thus far have not produced a sustainable solution. According to Barsoum, many photocatalysts typically require UV light treatment, which uses extensive energy. The impact of the new nanofilament resides in its self-sensitization behavior, which makes the nanofilament more sensitive to visible light.

"The use of visible light -- light the human eye can see -- like the sun or other simulated light sources, could significantly reduce the financial and energy consumption costs associated with treatment, while still being highly effective at removing dyes from wastewater, eliminating the toxic effluents," said Adam Walter, a doctoral student in Barsoum's research

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group, and the first author on the paper, in the Department of Materials Science and Engineering. "This also presents an exciting opportunity for expansion into other fields like solar cells or optical devices."

The result: cleaner water without the use of additional toxins or additional energy.

Science Daily, 10 October 2023

https://sciencedaily.com

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