

Current Science Reports

Tarnishing the Taj Mahal

Acid rain not to blame?

Acid rain, due to air pollution from industries and vehicles, is commonly blamed for the yellowing of the Taj Mahal. However, the process of discolouration is slow and difficult to simulate. And exposure for a short period fails to give a clear idea. So, how do we study the phenomenon?



Image: Joel Gordon via Wikimedia Commons

Researchers from the National Metallurgical Laboratory, Jamshedpur, the Central Pollution Control Board and the Indira Gandhi National Center for Arts, Delhi used metals as proxies to study how air pollutants affect corrosion. They took samples of carbon steel, zinc and copper and exposed them to the environment of the Taj Mahal from 2006 to 2010. To track the environment conditions during this period, the researchers used meteorological data from the India Meteorological Department and pollution data from the Central Pollution Control Board. Sulphur dioxide, nitrogen oxides and particulate matter were the major pollutants in the atmosphere.

Contrary to expectation, the pH of the rain was between 5.6 to 7.2, which does not fall under the category of acid rain. The rainwater had high concentrations of sulphates and ammonium ions, which mainly come from human activities.

The researchers analysed corrosion products on the metals using Raman spectroscopy and X-ray diffraction. Oxides and sulphides were the main constituents. Oxides form when metals are exposed to oxygen in the air. Reaction with acid rain forms sulphates and nitrates, but not sulphides, say the researchers.

The rate of corrosion was higher for copper than for zinc. This was unusual

as zinc corrodes faster than copper in an industrial environment.

If not industrial pollutants, what could be corroding the metals to form sulphides? The researchers attribute the corrosion and the formation of sulphides to hydrogen sulphide. The gas could come from the Yamuna flowing beside the Taj Mahal. The river has low flow and is full of effluents from industries and sewage. The sewage is decomposed by bacteria, releasing hydrogen sulphide, whose foul smell wafts down to the Taj Mahal.

'The gas corroding the experimental metals can also affect other building materials,' argues Jitendra Kumar Singh, National Metallurgical Laboratory.

To study the direct effect on Taj Mahal marble, exposure of at least 10 years is required. However, if hydrogen sulphide is the real culprit, municipal authorities will need to re-examine regulations on dumping sewage into the river to keep the Taj Mahal untarnished for the next generation.

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Fluoride Exposure in West Bengal

Cropping the risk

About one-third of the districts in West Bengal are affected by fluoride contamination. There is high fluoride content in groundwater and soil there. Soil types, geographical conditions and arid to semi-arid climatic conditions in the western parts of the state encourage high accumulation of fluoride in soil. The high soil fluoride, compounded with the fluoridated groundwater used for irrigation, facilitates fluoride accumulation in crops.

Recently, Tarit Roychowdhury and others from Jadavpur University, Kolkata assessed fluoride health risk in different crops grown in the region.

For analysis, they collected fresh food crops and soil samples from the highly fluoride-contaminated Purulia and Bankura districts. The crops consisted of cereals, pulses and non-leafy and leafy vegetables. Non-leafy and leafy vegetables, the team found, accumulated more fluoride than cereals and pulses. About 56% fluoride intake

from food came from non-leafy vegetables.

'The bioavailability of fluoride in root crops is very high. Onions have the highest fluoride accumulation,' says Tarit Roychowdhury.

The team carried out a health risk assessment for all age groups. They analysed the risk to children, adolescents and adults. The result indicates that there is no risk of fluorosis through individual food crops. But inhabitants in the region are vulnerable to fluoride exposure over their lifetime and are at risk for fluorosis, though not as much as to lead to cancer.

Proper watershed management for retaining fresh water, and limiting cultivation of crops to those that accumulate less fluoride, can help reduce long-term exposure to fluorides and related health risks.

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Asansol, West Bengal

Groundwater contamination

Asansol covers a vast spectrum of coalfield and industrial activities. To understand how industrial activity impacts groundwater quality, Gourisankar Panda and team from the Asansol Engineering College collaborated with researchers from other institutes.

They collected groundwater samples, pre- and post-monsoon. Groundwater there is neutral to slightly alkaline. After the monsoon, dissolved solids increase due to dissolved minerals, leaching and runoff water.

Atomic absorption spectrophotometry revealed lead and copper within permissible limits. Concentrations of other metals such as iron, cadmium and chromium were higher than safe before and after the monsoon.

Chromium, cadmium and lead levels can increase the chances of kidney damage. There is also a risk of cancer due to exposure to cadmium and lead.

Statistical analysis revealed that heavy metals in groundwater are derived primarily from industrial discharge, mining activities and leachate from solid waste disposal sites. Geogenic sources such as weathering of

bedrock, soil erosion, and soil–water interaction, were not significant.

Besides ensuring freshwater supply in the affected region, the municipal corporation, industrialists, the scientific community and other stakeholders must take action to address ground-water contamination.

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Rare Auto-inflammatory Disease

Treatable with repurposed drugs

A seven-year-old boy from an Indian family is suffering because of his own immune system. The boy has inflated blood vessels, seizures and arthritis due to auto-inflammation. This rare genetic disorder is due to marriages between blood relatives.

In collaboration with researchers from other countries, Pallavi Pimpale Chavan and Raju Khubchandani, SRCC Children's Hospital, Mumbai recently found the root cause of this syndrome.

Besides India, marriages between blood relatives occur in other countries also. The team found four such cases. By sequencing the whole-exomes of the four people, they identified mutations in a protein, TANK-binding kinase 1, as common factor.

'The condition develops when copies of the mutated gene are passed down from both parents,' says Pallavi Pimpale Chavan. 'This causes total loss of the function of the protein.'

TANK-binding kinase 1 is responsible for activating the body's defences against viruses. So people with this syndrome are vulnerable to a great range of viral infections.

Surprisingly, none of the four patients suffering from this syndrome exhibited insufficient antiviral immunity. Instead, they all had an auto-inflammatory condition. This is due to the tumour necrosis factor, a small signalling protein released by white blood cells to alert the immune system to induce inflammation and cell death.

Tumour necrosis factor is regulated by TANK-binding kinase 1. However, the loss of activity of the protein renders cells over sensitive to the tumour necrosis factor, which causes inflammation and triggers cell death in surrounding tissues.

'This genetic defect can be treated using the existing anti-tumour necrosis factor drug approved by the Food and Drug Administration,' says Raju Khubchandani.

A recent study found that deletions in TANK-binding kinase 1 make individuals more susceptible to COVID-19. COVID-19 also induces auto-inflammation by increasing interleukins. Therefore, identifying mutations in the TANK-binding kinase 1 using genetic testing can help in identifying COVID-19 susceptible individuals. Such people might benefit from special protective measures and repurposing of anti-tumour necrosis factor drugs.

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Peppermint Oil-loaded Microbeads

Curing stomach issues

Peppermint oil is a common remedy for abdominal pain and gas. But the oil is volatile and rapidly loses therapeutic value. Can we encapsulate it at lower temperatures to reduce volatility? To check, Bappaditya Chatterjee, from the Shobhaben Pratapbhai Patel School of Pharmacy and Technology Management, Mumbai collaborated with researchers from Malaysia, Iraq, the US, and China.

Using ultrasonic vibrations, the team created an emulsion of peppermint oil, alginate, a biocompatible polymer from red seaweed, and lecithin, an emulsifier. The emulsion was loaded into a syringe. The researchers applied high voltage and ejected the emulsion from the syringe. This electro-hydrodynamic atomisation formed microbeads. Using a scanning electron microscope, the researchers found that the microbeads were spherical and porous.

They calculated the microbead's encapsulation efficiency. It was 98%. They found that the microbeads shrink in acidic conditions but swell at alkaline pH, suggesting efficient delivery in the intestine.

To investigate how the microbeads were distributed in the gastrointestinal tract, the researchers fed mice microbeads with fluorescent dye. Observing fluorescence under UV, they found that almost 86% of the microbeads reached the intestines. The microbeads adhered to the gastrointestinal tract.

The team then induced irritable bowel syndrome in another set of mice and gave them peppermint oil-loaded microbeads. The microbeads suppressed the action of IL-1 β , a cytokine that produces an inflammatory response. They also upregulated IL-10 which helps reduce inflammation.

Preparing the microbeads to encapsulate peppermint oil is easy and economical. If they help reduce inflammation of the intestines, a common condition, peppermint oil producers and pharma companies need to step in.

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Antibiotic Resistance

Klebsiella pneumonia

Klebsiella pneumoniae normally live in our intestines. But, in other parts of the body, the microbe can be dangerous and cause severe infections. So the development of antimicrobial resistance among this species of bacteria is a major concern, especially in low- and lower-middle income countries.

Data on the occurrence of genes responsible for antibiotic resistance can help us identify the prevalence of drug resistant strains of *K. pneumoniae*.

Recently, researchers from the Cochin University of Science and Technology used this principle to conduct a global surveillance of antimicrobial resistance among *K. pneumoniae* strains in low- and lower-middle income countries.

They searched for antimicrobial resistance and virulence genes in 2500 strains of *K. pneumoniae* from the National Center for Biotechnology Information – a genetic database maintained by the United States National Library of Medicine. Most strains of *K. pneumoniae* had resistance genes.

The researchers plotted whole-genome data of the isolates on a global map using ArcGIS software. Sorting country-wise abundance of each antimicrobial gene, they found genes resistant to eleven antibiotic classes. About 150 variants of *K. pneumoniae* showed high resistance to the beta-lactam class of antibiotics.

The team screened the bacterial strains for commonly used antibiotics against *K. pneumoniae*, such as carbapenems.

'We found carbapenem-resistant strains in about 20 countries, mostly in Asia. The most affected are India, Pakistan and Vietnam. In India, such genotypes are higher by about 40 per cent,' says Reshma Silvester, CUSAT.

To control the situation, clinicians need to be more judicious in prescribing antibiotics. And we need research on alternative approaches to treating bacterial infections. Alternative approaches such as bacteriophage-therapy, vaccines and bacteriocins to control antibiotic resistant microbes are already on the scientific horizon.

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Eggshell Hydroxyapatite *Potent biocompatible material*

There is a high demand for hydroxyapatite, a calcium phosphate mineral used as bone filler and for dental applications. But available sources are costly. Eggshells are cheaper raw material for producing hydroxyapatite.

So Venkatachalam Murugesan and team from the Periyar University, Tamil Nadu took clean eggshells to synthesise hydroxyapatite using microwaves – an easily accessible and cheap method.

'Hydroxyapatite adhered to osteoblast cell lines. So it would function better in tissue repair,' says Manju Vaiyapuri, Periyar University. 'The biological calcium carbonate in eggshells helps improve the properties of the biomaterial.'

The researchers found no toxic effect on human osteoblast cell lines. Instead, in fact, hydroxyapatite from eggshells had excellent antioxidant properties.

'More than a hundred billion eggs are produced per year in India. Eggshells are usually thrown away. Biomedical industries can use eggshells to produce hydroxyapatite and reduce costs for repairing bones and teeth,' says Girija Easwaradas Kreedapathy, Periyar University, Tamil Nadu.

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Zinc Oxide–Carbon Nitride *Degrade dyes in sunlight*

Zinc oxide is a widely used photocatalyst. The catalyst absorbs radiation and excites electrons which jump from the valence band to the conduction band. The excited electrons react with

oxygen and water molecules to form free radicals. The free radicals can oxidise dyes in textile effluent.

However, in zinc oxide, the gap between valence and conduction bands is wide. So, high-energy UV radiations are required for efficient dye degradation. How do we make this catalyst use visible light to degrade dyes?

Researchers from the SRM Institute of Science and Technology and the Vel Tech High Tech Dr Rangarajan Dr Sakunthala Engineering College, Tamil Nadu mixed zinc oxide with graphitic carbon nitride, which efficiently absorbs radiation in the visible region. Graphitic carbon nitride suffers from poor thermal stability and low catalytic efficiency when used alone.

The researchers synthesised zinc oxide by reducing zinc nitrate hydrate using sodium hydroxide. For carbon nitride, they condensed melamine at high temperature. The team mixed the two components in various ratios by vigorously grinding and heating them at 550°C.

Using X-ray diffraction and electron microscopy, they found that the composites had a mesoporous structure though neither component had a mesoporous structure individually. The porous structure contained more surface active sites and allowed easy separation of photo-excited charge carriers from the catalytic surface.

'In the composite, zinc oxide increased graphitic carbon nitride's thermal stability,' says H. Leelavathi, SRM Institute of Science and Technology.

The composites could absorb more sunlight and efficiently transferred charges. Encouraged by the photocatalytic properties in the visible region, the researchers used the composites to degrade methylene blue and rhodamine. The composite with zinc oxide and carbon nitride, in a 0.75 : 1 ratio, gave the best results. When irradiated with sunlight for two hours, the composite reduced textile effluent colour by 80%.

To check the treated water for toxicity, the researchers grew fenugreek. The seedlings grew better in the treated water than in untreated water.

Moreover, the photocatalyst can be reused. The team used the catalyst three times in a row and found that the

reaction time increased a little in the third cycle.

Textile industries should come forward to test the material at industrial scale.

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Jackfruit Peel Nanocomposite *Removing nutrients from water*

Fertiliser runoff from agricultural land enriches nutrients in rivers and lakes, promoting the growth of algae on water surfaces. This prevents the entry of sunlight, inhibiting photosynthesis in underwater phytoplankton. And some algae also release toxins into the water. Dead algae, decomposed by bacteria, further degrade water quality, producing a foul smell. Some bacteria also produce methane, a greenhouse gas.

To remove nutrients from water, researchers from the Graphic Era University, Dehradun recently developed a nanocomposite. To prepare the nanocomposite, they heated dried jackfruit peel and powdered it. The researchers reasoned that a nanocomposite of jackfruit peel powder with polysaccharides would have higher pore diameter and surface area for adsorption. So, they extracted polysaccharides from mushrooms and magnetically impregnated them with jackfruit peel powder.

When tested, the nanocomposite showed maximum nutrient removal efficiency at pH 4 to 6. Under this condition, in the lab, the nanocomposite removed 99% of phosphates and nitrates from water.

The researchers then tested the nanocomposite in a continuously flowing wastewater system. It removed up to 96% of phosphates and nitrates from wastewater.

'The jackfruit peel-based nanocomposite selectively removed phosphates and nitrates from wastewater even in the presence of competing ions,' says Brij Bhushan, Graphic Era University, Dehradun.

'The nanocomposite lost only 10 per cent of nutrient removal efficiency after six cycles of reuse,' says Arunima Nayak, his colleague.

The environment friendly nanocomposite is a cheap way to harvest nutrients from water. And can reduce water pollution.

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Carbon Quantum Dots From waste polyethylene

Carbon quantum dots, thin graphite sheets, are useful as photocatalysts and as biosensors in diagnostics. The material is also used in optoelectronics and imaging. To synthesise carbon dots from polyethylene, potassium permanganate is used – a process in which manganese dioxide is a by-product, toxic and difficult to recover.

Researchers from IISER Mohali and NCL Pune recently came up with a safer and cheaper process to prepare carbon quantum dots.

They collected waste polyethylene sheets from IISER Mohali campus. Small bits of the plastic sheets were dropped into sulphuric acid. With heating and constant stirring, hydrogen atoms from the polymer chains were removed. The carbon atoms in the linear carbon chain were spontaneously transformed into cyclic graphitic carbon.

To this black material, the researchers added hydrogen peroxide to oxidise it. The resulting red transparent liquid was filtered. The filtrate was extracted using ethyl acetate. After removing moisture and drying, a powder of carbon quantum dots material remained.

The ability to absorb visible light and the copious amounts of oxygen available on the carbon quantum dots made the material an efficient photocatalyst, as demonstrated by the photo-oxidation of benzyl alcohol in the lab.

'The catalyst is specific to aromatic compounds. It had no action on aliphatic compounds,' notes C. P. Vinod, CSIR-NCL Pune.

Tests suggested that, when light is available, the material is able to use

oxygen in air or water and so, purging with oxygen is not necessary as is the case with other photocatalysts.

When the researchers tested the material for degradation of the dye, Rhodamine B, they found that the efficiency was 5 to 10 times more than with other catalysts!

'After the reaction is over, if the carbon quantum dots in the solution are left exposed to light, they will self-oxidise to form CO₂ in the solution. So there is no need for any elaborate process of removing the catalyst. A kind of autophagy of sorts,' says Sanjit Mondal, IISER Mohali.

'To make the carbon quantum dots we use waste polyethylene; we don't use potassium permanganate. So there are no toxic by-products; the product is highly efficient, better than other photocatalysts; you can keep reusing the product or you could just let it vanish into thin air; what more do you need?' asks Ujjal Gautam, IISER, Mohali.

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Paper Retractions Patterns and citations

In academic publishing, retractions are usually a consequence of either mistakes or misconduct in research. However, the retracted publication also gets citations. What happens to such citations? Are they also retracted?

To find out, Kiran Sharma from the BML Munjal University, Gurugram investigated patterns of retractions from 1981 to 2020 through team size and retracted citations. She extracted retracted papers indexed by the Web of Science and found about 12,000 retracted publications in the database. Retractions were highest from research areas such as biochemistry, molecular biology, oncology, ecology and energy.

She found a correlation between the number of authors and retractions. Some authors were repeat offenders with a large number of retractions. The retraction rate is higher in smaller teams. However, with bigger teams, retractions seem to reduce.

'Of course, this needs to be interpreted in the context of team strength distribution in the scientific community,' says Kiran.

Kiran then looked into papers with at least one citation and found about 7000 publications.

What happens to the citations when a paper is retracted? To find out, Kiran collected data on retracted citations received for the 7000 publications and found that about 3000 publications received at least one retracted citation.

Retracted citations increased from 1981. But, after 2017, there is a decrease in the count of retracted citations.

Analysing patterns of citations received by the retracted publications, Kiran noted that about 30% of citations are retracted. Most retracted citations are self-citations.

Citations are received for retracted papers because the researchers who cited the papers are not aware of the retraction of the cited paper. Researchers should not only verify sources when citing publications but also respond to retractions by retracting the citations.

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