

Science Last Fortnight

Himalayan Weathering

More silicate flow to the Ganga

Ever since the Himalayas emerged, some 70 to 40 million years ago, the chemical weathering of silicates has acted as a carbon sink. At higher temperatures, the weathering of silicates increases. This leads to increased removal of carbon dioxide from the atmosphere. This, in turn, leads to cooling. The magnitude of this negative feedback on the earth's temperature depends on the ratio of calcium and sodium in the water that carries carbonates to the sea. Moreover, if the weathering is too fast for the chemical reactions, only a fraction of the carbon dioxide is thus trapped. These introduce uncertainties into our understanding of the geological processes.

Recently, a team of scientists from the Jamia Millia Islamia, the University of Cambridge, the Université de Lorraine, France and the Fargau-Pratjau, Germany examined the output of chemical weathering from the Ganga flood plains. The Ganga begins its journey from Gangotri in Uttarakhand, 10,200 feet above sea level. The active flood plain of the Ganga – the area on either or both sides of the river, which is periodically flooded – begins from Haridwar and continues till Farakka.



Image: Wikimedia Commons

The researchers collected water from rivers in the Ganga flood plain and from some major rivers rising in the Himalayas as well as from the southern tributaries of the Ganga.

The samples were collected from river banks, or under bridges or from boats.

The team focussed on regional variations in flood plain river chemistries – the extent of precipitation of secondary carbonates in the flood plain and the quantification of chemical inputs from rain and erosion, and weathering of carbonate and silicate minerals.

The researchers report that chemical weathering in the floodplain is more than double that of the rapid erosion and chemical weathering in the Himalayas. They found that flood plain weathering supplied up to 63 per cent of the flux of positively charged ions of sodium, potassium, calcium, magnesium and strontium. At Farakka, the alkaline flux was 58 per cent.

In comparison, the weathering by Himalayan rivers was only 24 per cent and that by the southern tributaries was 18 per cent. The scientists used sequential leaching of floodplain bedloads to determine the compositions of the carbonate and silicate components of the sediments. They found that the bicarbonate flux, resulting from the weathering of silicate minerals, causes long-term removal of carbon dioxide from oceans and the atmosphere, by precipitating the carbonate minerals in the oceans.

Thus, the researchers conclude that the weathering of the Ganga flood plain also makes a dominant contribution to the material eroded. As the weathering of the flood plain also supplies chemical fluxes to the oceans, these results have significant implications for our understanding of the contributions of the continent to climate stabilisation.

J. Geochim. Cosmochim. Acta, **225**: 146–175

Cleaning Textile Effluent

Electro-catalytic oxidation

Wastewater from the textile industry is complex. It contains metals, salts, fabric softeners, pesticides, surfactants, polishing, bleaching, fixing, anti-

wrinkle, coupling and coating agents. Releasing the effluents is, therefore, detrimental to aquatic ecosystems. The Central Pollution Control Board has made it mandatory for textile industries to set up in-house effluent treatment technologies to attain zero liquid discharge.

Existing effluent treatment approaches are time consuming, energy intensive and are not effective in removing non-biodegradable synthetic dyes. Researchers from the Thapar Institute of Engineering and Technology, Punjab, now suggest a solution: an electro-catalytic oxidative reactor to treat the non-biodegradable part of textile effluents. They prepared a model reactor, using titanium coated with ruthenium oxide, as anode and aluminium as cathode.

The researchers first determined the pH, biological and chemical oxygen demand, total dissolved salts and the colour of a sample of textile wastewater. Then, they continuously pumped the effluent into their model reactor. The team found that the effluents could be treated in about 2 hours.

They simulated the process and, using model fitting and statistical analysis by regression, they found that the actual and simulated responses were highly correlated. This simplifies the setting up of systems to monitor the electro-catalytic oxidation process in water-treatment plants.

Next, using GC–MS and UV spectrophotometric analysis, the team confirmed that fabric softeners, dyes, and polymers degrade into chlorinated and other transformed compounds. The researchers propose a detailed mechanism to deal with oxidation events and the degradation mechanism.

Performing a bioassay against a common freshwater fish, *Aplocheilus panchax*, the team found that the treated effluent had reduced toxicity.

What is more, using scanning electron microscopy and XRD analysis, the researchers confirmed that the anodes are reusable as the morphology of the Ti/RuO₂ anodes was intact after the effluent oxidation process.

Such a cost-effective and efficient electro-catalytic process could be used by textile factories to meet the stringent conditions set up by pollution control authorities.

J. Hazard. Mater., **346**: 242–252

Enhanced Chromium Recovery From tannery effluent

Chromium, as pure metal, has no adverse effects. However, its toxic trivalent form causes dermatitis and bronchial carcinomas. This form of chromium is a major constituent in tannery effluent.

Recently, a team from the CECRI, Karaikudi and the CLRI, Chennai developed a simple membrane electrochemical reactor to recover chromium from tannery effluent. Where earlier techniques used surfactants and coagulating agents to recover chromium, the team claims that their method employs organic compounds already present in tannery effluents.

The electrochemical cell was fabricated using solid polypropylene. The cell had two chambers separated by a cation exchange membrane, to allow proton flow. One chamber has Ti/TiO₂-RuO₂ as anode and the other, Ti as a cathode. The team took H₂SO₄ as anolyte and tannery effluent as catholyte.

During electrolysis, the protons flowed from anolyte to catholyte, reducing the pH of the effluent. The hydroxyl ions, produced by the cathode, were absorbed by protein-lipid complexes, in the catholyte. The protein-lipid complexes act as coagulating agents. These negatively charged alkaline complexes absorb the positively charged trivalent chromium and form insoluble complexes, say the scientists.

The team observed that the hydrogen and oxygen evolving from the cathode lift this insoluble chromium complex to the top as foam, which can be collected easily. Thus, there was no need for any external addition of surfactants.

The initial concentration of trivalent chromium, in the tannery effluent, was 2000 to 5000 mg l⁻¹. After three hours of the process, the scientists recovered about 98% chromium.

They claim that this simple and effective technique for chromium removal from tannery waste could help tanning industries comply with Pollution Control Board directives. Moreover, the chromium thus recovered can also be reused in tanning, making investments cost-effective for leather industries.

J. Hazard. Mater., **346**: 133–139

Low Energy RO Membrane For low cost desalination

Reverse osmosis uses membranes for desalination. The properties of these membranes greatly impact productivity and costs. So, scientists have been working to develop high-performance RO membranes.

Recently, scientists from the CSIR-Central Salt and Marine Chemicals Research Institute, Gujarat, reported developing a reverse osmosis membrane that requires very low energy inputs, to reduce the cost of desalination. To make the membrane, they experimented with different concentrations and combinations of polyamide and chitosan. They used glutaraldehyde to modify the surface of the membranes. They found that glutaraldehyde effectively cross linked the supramolecular assembly formed by chitosan. This increased salt rejection.

The researchers observed that the contact angle of the modified membrane declined significantly, increasing hydrophilicity. They also noted that the membrane had increased surface roughness and area ratio. They say that these properties are responsible for increased water-flux.

By optimising and fine-tuning this method, an ultra-low energy RO technology based on a polyamide-chitosan-glutaraldehyde membrane can be further developed for commercial application of this invention for desalination.

J. Appl. Poly. Sci., **135**(10): 2017

Eco-Friendly Nanoparticles Guava leaves degrade synthetic dye

Synthetic dyes, from the textile industry, are discharged as wastewater. They contain harmful chemicals. Existing electrochemical and electrolytic methods require electrical energy in-

puts, increasing costs. So, researchers are actively investigating photocatalysis using nanoparticles to reduce operational expenses.

Last fortnight, scientists from the Sri Guru Granth Sahib World University and the Thapar University reported efficiently using eco-friendly SnO₂ nanoparticles as photocatalysts. SnO₂ has high electron mobility, ensuring faster photocatalysis.

Preparing nanoparticles by conventional methods such as the sol-gel technique, electrodeposition, chemical vapour synthesis, and mechanical attrition is complicated and not too eco-friendly. The team worked around the issue by using guava leaf extract to make SnO₂ nanoparticles.

To obtain the extract, the scientists ground sun-dried guava leaves. They heated the ground leaves at 60°C and filtered the mixture, to which they added tin chloride. They converted the mixture into jelly by stirring it at 60°C and then at room temperature. The researchers calcined the jelly at high temperature to obtain SnO₂ nanoparticles.

They added these nanoparticles to a solution of vinyl disulphone, a yellow synthetic dye, and stirred the mixture for 30 minutes, in the dark, to establish an adsorption-desorption equilibrium in the reaction mixture. The team then exposed the mixture to sunlight for different time intervals and monitored the remaining concentration of dye using UV-Vis spectrophotometry. They found that the SnO₂ nanoparticles could degrade 90% of the dye in 3 hours in the presence of sunlight.

What is more, the photocatalytic activity remained constant even after using the same nanoparticles for up to five times, establishing reusability of the material. The report, thus, offers a simple method to prepare reusable and eco-friendly nanoparticles.

J. Mater. Lett., **215**: 121–124

Nanoparticles in Ecosystems Understanding the interaction

Nanoparticles have a wide array of applications. However, there is a hue and cry about tapping their full potential, due to their size. It is hypothesised that these small particles can enter

living systems and significantly alter biological mechanisms. So there is a need to understand the mechanism of nanoparticles in living beings.

Last fortnight, a team of scientists from the Tezpur University, Assam and the Visva Bharati Santiniketan, Kolkata conducted a study to understand the dynamics and impacts of silver nanoparticles at different concentrations in earthworm, microbe, plant and soil.

They mixed a plant extract of *Thuja occidentalis* with a mixture of silver nitrate and polyethylene glycol to synthesise the nanoparticle. They confirmed the size, silver content and the nature of the nanoparticle using TEM, atomic absorption spectrometry and BET analysis.

The nanoparticle was then fed at different concentrations to earthworms, maintained in a cow dung based substrate. The team measured fecundity, body weight and silver accumulation through histological analysis in both treated and untreated earthworms. There was a significant reduction in all the parameters but there was no apparent lethal effect in treated earthworms.

They also monitored soil properties and enzyme activities in response to the addition of silver nanoparticles at different concentrations. The pH level dropped and there was a decline in the bioavailability of nitrogen, phosphorus and potassium levels in the soil. There was a decrease in enzyme activity at week 72 where the concentration of silver nanoparticles was 50 mg kg^{-1} . This contributed to a decline in soil microbes.

Finally, the team used the treated soil to grow tomatoes. There was a drastic reduction in tomato yield at 10 mg kg^{-1} level. The result of this study can be the foundation for researchers to carry out future studies to figure out the long-term effects of manmade nanoparticles in soils.

Geoderma, 314: 73–84

Turmeric as Photosensitiser *Performance and stability analysis*

Better photovoltaic performance makes dye-sensitised solar cells increasingly attractive to researchers.

This performance depends not only on the photo anode, electrolyte, cathode, and solar radiation intensity, but also on the nature of the dye. Though there are many natural dyes, we are yet to explore the effectiveness of their molecules as photosensitiser to improve solar cell efficiency.

Recently, scientists from the Dr B. C. Roy Engineering College, Durgapur and the Shree Ramkrishna Shilpa Vidyalaya, Birbhum, reported investigating the use of turmeric as photosensitiser. They prepared dye-sensitised solar cells using zinc oxide as photo anode and turmeric stem extract as dye sensitiser.



Image: Wikimedia Commons

The team observed that the dye-loaded zinc oxide film showed a broad absorption band in the ultraviolet region. This extended up to the visible region due to the bonding of the dye with the zinc oxide surface. The researchers measured the voltage-to-current response using cyclic voltammetry to study stability and photoconversion efficiency. They noted that the dye has a wide band gap with high electron affinity. This confers long-term stability to the dye molecule due to a combined oxidation and reduction process in the presence of sunlight.

Though the power conversion efficiency of the cells sensitised with the dye was only 1%, compared to 15% per cent with other dyes, the turmeric stem dye is stable and has enhanced visible light to electrical conversion efficiency. So, the scientists claim that it is suitable for photovoltaic applications.

The efficiency of dye-sensitised solar cells with the natural dye is low because of the weak interaction between the semiconducting zinc oxide layer and the dye. Moreover, the dye molecules tend to aggregate on the photoanode film – another important factor which strongly affects efficiency.

If these limitations can be overcome, the long-term stability of the turmeric dye molecule could be leveraged for solar cell applications.

Spectrochim. Acta A, 193: 467–474

Barrier for Betterment *High efficiency solar device*

Perovskite-based solar devices have better efficiency than semiconductor dependent devices and they are cheaper to make. Scientists at the Marathwada University, Nanded in collaboration with Korean scientists now report improving the efficiency of such solar devices further.

Their perovskite-based solar device is made up of layers: a transparent, glassy conducting substrate made of fluorine doped tin oxide, a methylammonium lead iodide perovskite-based absorber layer, and a metallic back contact layer. Since the extraction and transport of electrons depends closely upon interface and energy levels, the researchers modified the interfacial layers. They deposited a few layers of zinc sulphite, using successive ionic layer adsorption and reaction between the mesoporous tin oxide conduction band layer and perovskite absorber layer. This, they hypothesised would block the backflow of electrons, and thus improve the power conservation efficiency.

The researchers used X-ray photoelectron spectroscopy and found intimate interfacial contact between layers, affecting microstructure of perovskite material. Instead of irregular projections there was a more crystalline appearance.

After adding a barrier between conduction and absorber layers, the scientists studied the process of electron transfer, using dark current and Mott-Schottky analyses. They recorded enhanced external quantum efficiency and current density value of the device along with improvement of open power circuit voltage and fill factor. These findings show that modified perovskite solar devices have a reduced energy barrier facilitating better electron transfer.

Photoluminescence and time-resolved photoluminescence spectroscopic

measurements showed that there is no hindrance in electron flow between the layers. The researchers found similar energy level alignment of conduction and absorber layers using ultraviolet photoelectron spectroscopy analysis.

Thus photo-generated electrons in the perovskite layer are captured efficiently by the mesoporous tin oxide layer. The zinc sulphite layer added in between by the scientists, resulted in higher bandgap energy, as shown by electrochemical impedance spectroscopy. It acted as a physical barrier to retard backflow of electrons and charge recombination. This improved the efficiency of the device.

The scientists made twenty devices with different composition and thickness of deposited layers and compared the devices using UV-visible absorption spectroscopic measurements. The best results were found when four cycles of deposition of ZnS was applied.

They found the process highly reproducible for making solar devices having similar specifications and performance. The modifications done by the scientists promise perovskite solar cells with a consistent high-performance compared to other interface modifications reported.

J. Alloy Compound, **738**: 405–414

Waste to Curb Waste

Plastic from nut shell and fruit peel

Plastics derived from petroleum have versatile applications due to their high stability. However, this also causes them to persist in the environment. Managing plastic waste thus becomes a challenge. Plastic packages are either burned or dumped, causing further detriment to the environment. Researchers are now exploring bio-based polymers as alternatives to petro plastic.

A team of scientists led by M. Sukumar from the Anna University, Tamil Nadu has now come up with a method to make bio-plastic from agriculture waste. In the past bio-based polymers have been prepared from tamarind seeds, mango kernel, pineapple leaves, rice bran and sugarcane bagasse. However, the supply

of raw materials did not match the demand and the method of extraction was tedious. Also, the polymers lacked adequate plasticity.

Sukumar and team selected the inedible shell of cashew nut and walnut to produce bio-plastic. They used cashew nut shell, a rich and easily extractable source of starch as a film forming matrix. The cellulose from walnut shell acted as reinforcing material. The scientists added citric acid to cross-link the starch and cellulose.

They, then, performed tests on the bio-plastic to assess its commercial viability. And found that it has high tensile strength, low oxygen permeability and moisture content. This makes it suitable for superior quality packaging film.

The bio-plastic was stable up to 220°C – perfect for the range of temperatures used in food processing and packaging. The addition of cellulose increased the thermostability of the matrix many fold. The solubility of the film in water was high, making it easily biodegradable.



Image: Jiumoni

To ensure its applicability for packaging fruits and vegetables, the team experimented further. Since cashew nut starch and walnut cellulose have limited antibacterial properties, the bioplastic would be susceptible to contamination. So the scientists added an extract of pomegranate peel – another agro waste product – to the bio-plastic, to enhance the antimicrobial property. Since the extract possesses antioxidant properties, storage and shelf life would also improve.

The team then tested the bio-plastic against six food pathogens. They report that the extract improved antibacterial property against all six.

The bio-based plastic is a cost effective and safe packaging material with superior plasticising properties. This alternative to petro plastic will reduce the threat to the environment.

Carb. Pol., **184**: 231–242

The Mystery of the Missing FRS *Story and History of Sir P. C. Ray*

Sir Prafulla Chandra Ray worked at the Presidency College in Calcutta and then at Calcutta University, to build a successful school of chemical research in India and even received Knighthood for his contributions to chemistry. He attracted bright and dedicated students, published more than 150 papers (in those days), mostly in English and some in German. He was the first Indian of that era to be nominated as Fellow of the Royal Society – in 1913. He was nominated again and then again and again. But he did not get to be a FRS.

Meanwhile, many other scientific giants in the country – H. J. Bhabha, J. C. Bose, S. N. Bose, C. V. Raman, M. N. Saha, ... – were nominated. And they became Fellows. Why? What were the personal, academic, political, procedural, social, cultural or historical reasons that could have prevented P. C. Ray from reaching the coveted honour?

Arnab Rai Choudhuri from the Indian Institute of Science collaborated with Rajinder Singh from the University of Oldenburg, Germany to examine the problem. Their findings were published last fortnight.

To paraphrase Santayana, those who do not study history are condemned to repeat it.

Notes Rec., **72**(1): 57–73

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