Science Last Fortnight

Duckweeds as Human Food
Wolfing down Wolffia

There are a large number of ponds in Kerala. And duckweeds grow plentiful in freshwater. They are known to be rich in proteins with essential acid composition close to WHO recommendations. Moreover, they contain omega-3 fatty acids, a neutraceutical of great value.

But then there are a large number of duckweeds. They belong to five distinct genera of the Limnacea family: *Spirodela*, *Landoltia*, *Lemna*, *Wolffiella* and *Wolffia*. Sowjanya Sree, at the Central University of Kerala, collaborated with German scientists to find out which is the best for human consumption.

The starch content of duckweeds ranged from 4% to 10%. But protein content was high – 20–35% per dry weight. Duckweed total fat is rich in the $n3$ α-linolenic acid, which results in low $n6/n3$ ratios. *W. microscopica* and *W. hyaline* had the highest amounts of essential acids. In comparison to other vegetarian foods, duckweeds also showed very high concentrations of antioxidants, lutein and zeaxanthin. Phytosterols, known to lower plasma cholesterol and LDL cholesterol, are also high – 5 times higher than in most other plant oils.

Duckweeds, especially species belonging to *Wolffia*, have been traditionally eaten in South East Asia as salad, mixed in soups or curries or in omelettes.

W. microscopica is the fastest growing angiosperm known till date. *Wolffiella* species has the potential to reduce protein and other nutritional deficiencies in the country, if the Indian public accepts these weeds as food items.

Food Chemistry, **217**, 266

Unified Marker
For detecting milk adulteration

In 2012, the national survey conducted by the FSSAI disclosed that 70% of milk adulteration occurs due to chemicals, detergents, skim milk powder and impure water. The identification of these adulterants is difficult because of lack of standardized techniques. Scientists from the Indian Institute of Technology, Hyderabad, Telangana, proposed a 'unified universal marker' for the detection of adulteration in milk.

The research team aimed at examining the inherent biophysical properties of milk for the detection of adulteration and for quality profiling. They collected fresh cow milk samples from several local sources and determined the initial threshold values for impedance and pH. They monitored the effect of multiple adulterants under electrical conductivity and pH simultaneously. They also performed spectroscopic studies using fabricated gold electrodes on glass substrate for developing a multiplex lab-on-chip miniaturized platform. It was found that parameters like electrical conductivity and pH were efficient as unified markers. However, the study required a 'safe range' estimate for each selected marker to develop a tamper-proof system.

Indeed, analysis through biophysical parameters acted as potential universal markers in comparison to the traditional adulterant-specific approaches. Perhaps, further studies will provide more insights.

Food Chemistry, **217**, 756–765

The Golden Solution
Testing water purity with gold

Malachite green is a dye which finds use in aquaculture due to its antimicrobial properties. Even at low levels, this dye is toxic to humans. But, due to low-cost and easy availability, it is still used by many aquaculture farms. Now, John and his student from the Gandhigram Rural Institute, Tamil Nadu, report a simple inexpensive technique to detect malachite green in water.

Gold nanoparticles possess remarkable optical properties and show strong surface plasmon resonance. As a result, solutions with different sizes of gold nanoparticles have different colours. For instance, a solution of small gold nanoparticles is usually wine red. But when these nanoparticles aggregate, they absorb longer wavelengths of incident light changing the colour of the solution to deep violet. The scientists made use of this property for devising a simple dye detecting strategy.

They capped the gold nanoparticles with 3,5-diamino-1,2,4-triazole to create stable amine functionalized nanoparticles. Addition of malachite green creates strong electrostatic interaction between the ammonium ion of the dye and the free amine group of the amine-functionalized nanoparticle. This induces aggregation. The colour of the amine-functionalized gold nanoparticle solution changes from wine red to deep violet. The colour change is so pronounced that it can be detected by the naked eye if the dye concentration is more than 25 micromoles.

Scientists also demonstrated the practical application of this technique in water collected from fish farms. The low-cost, rapid response time and simplicity make this method viable for routine monitoring of malachite green in aquaculture facilities.

Spectrochimica Acta Part A, **173**, 837–842

Geographical Identity of Basmati
Isotopes as tracing tools

Basmati holds a special place in the international market for its distinct aroma and superior flavour. The increasing demand for Indian Basmati in the global market has led to adulteration with rice from other regions. The geographical origin of rice can be established using multi-element patterns and isotopic composition. Indian Basmati, however, lacked such a database.

Last fortnight, R. A. Lagad and team, from the Physical Research Laboratory, Ahmedabad, reported the development of a database of $^{87}Sr/^{86}Sr$ ratio and rare earth element composition for Indian Basmati rice.

The team collected plant, soil and water samples from various localities of the Indo-Gangetic Plain. They analysed the composition of strontium, rubidium and rare earth elements in the plants and soils. There was significant variation in the concentrations of strontium and rubidium in rice samples and a strong correlation between the concentrations of rare earth elements in rice and in the soil in which it was grown.

The team also determined the isotopic ratio of strontium in rice grain, soil and water samples. The $^{87}Sr/^{86}Sr$ ratio of rice samples is within the range of authentic Basmati. The silicate fraction of the soil had a higher $^{87}Sr/^{86}Sr$ ratio than the carbonate fraction. Scientists also examined the possible source of strontium in rice plants. It appears that irrigation water is the main source of strontium in rice. Thus, the higher $^{87}Sr/^{86}Sr$ ratio in Indian Basmati rice is attributable to the river Ganga whose water is used for irrigation.

The scientists believe that the database on $^{87}Sr/^{86}Sr$ ratio and rare earth element composition would help identify Basmati of Indian origin. We can thus eliminate adulteration and help customers get genuine Basmati.

Food Chemistry, **217**, 254–265

Are you being Drugged?

Paper chip test for ketamine

Ketamine is used as anesthetic for children and as sedative for painful medical procedures. But, recently, the drug has been implicated in date rapes. To make matters worse, current methods for ketamine detection are time-consuming and expensive. Scientists have now found a way around this problem by creating an inexpensive paper-based microfluidic device.

In their model, Narang and Malhotra, from the Amity University, Noida, used a combination of zeolite nanocrystals and graphite oxide nanoflakes as detectors and connected it to carbon ink printed electrodes. The pattern for the entire assembly was first created as a stencil and then printed on Whatman paper. Next, the setup was tested for ketamine detection using electrochemical method.

Liquids containing different quantities of ketamine were added to the zeolite-graphite oxide nano-detector and voltage was varied from –2 to +2 mV to detect the current produced from the electrodes. Liquids with a higher amount of ketamine produced greater current flow. The device was found to be extremely specific for the drug and could detect quantities in the range of 0.001 to 5 nM/ml.

Most established methods for drug detection are based on changes in pH and can be affected by environmental conditions. Since this method is based on electrochemistry, it has greater sensitivity. Additionally, the paper chip is economical, stable for almost two months and can be reused without any significant loss in performance. Scientists are confident that this device will greatly improve ketamine detection, especially in developing countries.

Biosensors & Bioelectronics, **88**, 249–257

Nanodetection of Insecticides

Insecticides are applied to plants for increasing productivity. Most of the pesticides applied are not easily degradable. They persist in soil, leach to groundwater and surface water and contaminate the environment. Depending on their chemical properties, they can enter the organism, accumulate in food chains and, consequently, influence health. Some pesticides still defy detection because existing methods are costly and time consuming.

Terbufos and thiacloprid are harmful insecticides extensively used for agriculture. Conventional methods of detecting these insecticides are used at high concentrations and drastic reaction conditions. Detection using these methods also suffers from various interferences which makes the screening difficult.

Last fortnight, Kailasa and team, from the S. V. National Institute of Technology, Surat, formulated a simple colorimetric method for the selective detection of terbufos and thiacloprid insecticides. They used gold nanoparticles with a nitro and hydroxy benzylindole-dithiocarbamate derivative, a red coloured aggregate, as probe.

The team collected tap, river and canal water samples from the Department of Applied Chemistry, the Tapi River and the agriculture canal, Surat, India. They spiked these samples with various concentrations of insecticides. They also used corn, sorghum, tomato and apple samples, fortified with different concentrations of insecticides, for the experiment. When tested on these samples, the probes turned from red to blue.

In food and environmental pollution control laboratories, this serves as a simple, selective and sensitive colorimetric method for detecting even trace amounts of terbufos and thiacloprid contaminants.

Colloids and Surfaces, **515**, 50–61

Hibiscus Leaves

Potential for pigments

Inorganic materials used in photonic and optoelectronic devices have large nonlinear refractive index. But they require expensive and high power lasers to provide nonlinear optical effects. Therefore, natural dyes and organic molecules are being investigated for their potential use in nonlinear optics. Naturally occurring dyes like chlorophyll, carotenoid, etc. have a large nonlinear refractive index and can provide nonlinear optical effects with low power lasers. Hence, they are better alternatives to the inorganic materials that are already in use.

Last fortnight, scientists from the National Institute of Technology, Durgapur, extracted a natural pigment, with high nonlinear refractive index, from an evergreen plant: *Hibiscus rosa-sinensis*. The scientists extracted pigments from the leaves by column chromatography. UV-Visible absorption spectroscopic analysis revealed that the extract contained 56% chlorophyll-*a*, 25% chlorophyll-*b* and 19% carotenoid.

Analysis of photoluminescence intensity showed that the extracted pigments exhibit stable photoluminescence emission characteristics.

The researchers examined the nonlinear optical properties of the natural pigment by spatial self-phase modulation using a low power CW He–Ne laser of wavelength 632.8 nm, with a maximum power of 5 mW as pump light. The nonlinear refractive index of the pigment extract was 3.5×10^{-5} cm^2/W. This value is larger than even those of some 2D materials, such as MoS_2, $MoSe_2$, etc., reported earlier! This property is attributed to the asymmetrical structure of chlorophyll, molecular reorientation and thermally induced nonlinearity in the sample.

This work opens new avenues for the economical synthesis of organic dyes with large nonlinear optical properties. They are promising candidates for use in optical communication, data storage, optical limiting devices, etc. With their high value of nonlinear refractive index and photostability, these pigments can be used in nonlinear optical microscopy to stain biological molecules for improved imaging contrast.

Spectrochimica Acta Part A, **173**, 400–406

Lens-Free Real-Time Imaging

Detecting toxic aluminium

Aluminium is the third most abundant metallic element in the lithosphere. Accumulation of aluminium in the body causes neurotoxicity and is implicated in the development of Alzheimer's and Parkinson's diseases. It also causes amyotrophic lateral sclerosis and chronic renal failure. The detection and quantification of aluminium have been a problem due to the strong hydration capacity of aluminium in aqueous media. This leads to weak coordination among aluminium molecules. *In vivo* detection of aluminium in the biological system is even more difficult.

Lens-free real-time live cell imaging is a simple, non-invasive method for assessing the biological activities of different elements. Last fortnight, researchers at the North Eastern Hill University, Meghalaya, reported the development of a new coumarin-based Schiff base compound as a probe to detect aluminium in living cells. They synthesized the coumarin-based Schiff base by adding salicylaldehyde dropwise to 3-amino-4-hydroxycoumarin. This compound reacts with aluminium and forms a stable aluminium coumarin-based Schiff base complex. This stable complex was non-toxic to cells.

The coumarin-based Schiff base has high selectivity and sensitivity towards aluminium. Therefore, researchers were able to successfully quantify the levels and activity of aluminium in HeLa cells using real-time live cell imaging. In real-time imaging, the colour change from light yellow to colourless and the appearance of blue fluorescence was visualized with the naked eye. Using this method, aluminium concentrations as low as 1.34 μM could be detected in the intracellular region.

Lens-free imaging easily detects aluminium levels in the intracellular region and in live cells. Thus, it helps diagnose aluminium-induced toxicity. It also helps count red and white blood cells as well as proliferating cancer cells. Moreover, it is low cost.

Spectrochimica Acta Part A, **173**, 537–543.

Fungal Biofactory

For quantum dot synthesis

Heavy metal pollution is a serious environmental problem. Fungi are known to tolerate and detoxify metals. Jaya Mary Jacob and team at the NIT, Karnataka, now find that, while removing lead from the environment, fungi can also synthesize lead selenide quantum dots (PbSe QDs).

The team used a marine fungus, *Aspergillus terreus*, to study the mechanisms of metal detoxification. This fungus expresses a pathway for PbSe QD biosynthesis. This biosynthesis was confirmed using UV–Vis fluorescence spectroscopy.

The researchers also observed an increase in the total protein content. Results show higher levels of metallothionein in samples after the biogenesis reaction. This affirms the active role of these metal binding proteins in PbSe QD synthesis.

The scanning electron micrographs of the fungal biomass before and after biosynthesis of PbSe QDs showed characteristic surface roughness and agglomerations. The scientists found that the secreted proteins play a vital role in the extracellular co-precipitation of metals.

The fungus releases phytochelatins, metallothioneins and superoxide dismutases, whose function is to scavenge Reactive Oxygen Species. These results suggest that oxidative stress plays a major role in *A. terreus* for the synthesis of PbSe QDs.

This study clarifies the cellular mechanisms involved in the detoxification of toxic heavy metals by the fungus, *A. terreus*. Moreover, it provides an economical and eco-friendly technique for QD synthesis.

J. Hazardous Materials, **324**, 54–61

Ground Support for Titanium

Molding metal–clay catalysts

Titanium oxide is used as a catalyst for the photodegradation of harmful organic chemicals. But it has small surface area and, therefore, low adsorption capacity for organic compounds. It is also difficult to recover from solutions. This impedes its use in industries. Now, Basu and team, from the Thapar University, Patiala, use clay – an age old water purifier – to boost the activity of titanium oxide nanoparticles.

To improve titanium oxide function, the scientists created titanium oxide–clay nanocomposites. Clay has high porosity and can adsorb a wide variety of pollutants. The scientists worked with three types of clay: Bentonite, Kunipia-F and Kaolin clay. A suspension of clay nanoparticles was mixed with titanium oxide and stirred in a microwave to form titanium oxide–clay nanocomposites. These were then washed, characterized and studied for photocatalytic action.

The researchers found that Bentonite and Kunipia, rich in silica, form composites that are smaller in size and exhibit higher light absorption intensity. The action of titanium oxide–clay nanocomposites was then compared with Degussa P25 – a commercial titanium oxide photocatalyst – for the ability to degrade methylene blue and chlorobenzene in water.

Results show that titanium oxide–clay nanocomposites are better at cleaving organic pollutants. However, titanium oxide–bentonite nanocomposites were found to be five times more efficient in degrading methylene blue, and eight times as effective as Degussa P25 in cleaving chlorobenzene.

Given their superior action, easy preparation and high recovery, scientists are confident that bentonite-titanium–oxide nanocomposites will find wide scale use in industry.

J. Alloys and Compounds, **694**, 574–580

Titanium in Solar Cells

Better way to deposit

Dye-sensitized solar cells mimic plants. Like chlorophyll in green leaves, the organic dyes of these solar cells absorb light. This generates photoexcited charges. There is a coat of titanium dioxide nanoparticles on the surface of these cells. The titanium dioxide separates these photoexcited charges and passes them to suitable materials, generating voltage.

Titanium dioxide nanocrystals, thus, play an important role in dye sensitized solar cells. Depositing a thin film of titanium dioxide nanocrystals over solar cells is, therefore, a critical step. Creating a defect-free crystalline film is tricky. Gaikwad and team, from the Shivaji University, Kolhapur, have now come up with a better method for depositing titanium oxide.

They used a series of adsorptions and ionic reactions to deposit the TiO_2 film over the glass substrate. First, a layer of titanium–water complex is formed which is washed with double distilled water. This removes the loosely bound particles. Then the substrate is treated in a basic medium which forms stable TiO_2 on the surface. Finally the substrate is rinsed again to remove loose TiO_2 particles.

The team reports that this method of deposition improves the crystallinity and electronic nature of the TiO_2 layer. The layer is homogeneous and has fewer defects. This leads to restricted recombination which improves the current density. The best part: the method is cheap and works for large area deposition.

The recipe to print solar cells with the highest efficiency is not complete. Scientists continue to tweak to increase the conversion, even if by mere decimals. Each tweak takes us one step closer to utilizing solar energy to its fullest.

J. Colloid and Interface Sci., **488**, 269–276

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