

# Investigations in Energy and Environmental Research

(2001 to 2023)



by

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## Preamble

It gives an immense pleasure to bring out this mini-book in which overall investigations performed by me in the exciting areas of energy and environment is outlined. The book presents the summary of cutting-edge research carried in the domain of energy and environment. It reflects the scientific journey from Post-doctoral researcher (2001) to Professor and Director of School of Energy and Environmental Systems, DIAT (2023).

It is important to note that the investigations presented are mainly as first author (Table Researcher) or corresponding/ chief author. The work summarizes the contribution in energy domains such as hydrogen, rocket fuels, nuclear, biofuels, solar energy materials and waste to energy. Further, an exposure in environmental areas includes treatment of highly toxic pollutants (dioxins, pesticides, hazardous metals, explosives), desulphurization of fuels and CO<sub>2</sub> capture. Some of these studies have been scaled from laboratory to pilot scale research. Here in, the synopsis of each investigation undertaken is given and for further details, it is requested to refer the references. The notable investigations are mainly carried out in prestigious national and international organizations such as DIAT, Pune; ICT, Mumbai; BARC, Mumbai; ENEA, Italy and IST, Portugal.

In every research project, sincere efforts were made to perform the investigation at highest scientific level with full ethics. It therefore fetched high impact publications and patents and gave recognition as top 2% Scientist of the world (Stanford University, USA report). Finally, I wish to deeply acknowledge my PhD research supervisor (Prof. V.V. Mahajani), Fellow scientists of EU, Collaborators from DRDO and Industry, Funding agencies, Research Students and the Almighty.

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## ENERGY RESEARCH

### 1) Safe Hydrogen Usage

[Place: Defence Institute of Advanced Technolgoy (DU), Ministry of Defence, Pune, India]

The energy demand of the world is continuously increasing. The conventional energy sources are limited, non-renewable and give rise to the enormous amount of pollutants. The need of the time is to use renewable and clean energy sources due to the reducing sources of fossil fuels and pollution problems. Hydrogen gas is always considered as potential energy carrier (high gravimetric energy density: 120MJ/kg) due to its smooth production and pollutant free combustion, which has quite an ability to replace conventional energy sources. However, there are safety concerns over hydrogen handling and storage. The main limitations in use of hydrogen for various applications are - ease of leaking during storage due to low molecular size, embrittlement of metals, high flammability and explosive range (4-75% by volume in air). Further, its low ignition energy (0.019 mJ), may lead to accidental burning and explosion. Hydrogen burns with a nearly invisible flame that poses other severe problems in fire prevention and safety.

The inhibition or total suppression of hydrogen flames can be achieved by addition of various inhibitors or suppressors. Addition of chemical inhibitors influence the flame propagation in three ways: by altering the proportion of unburnt mixture so as to affect heat conduction or radical diffusion, by changing flame temperature, by specific chemical inhibition of combustion reactions. Various halogenated compounds has been studied for their inhibitory effects on hydrogen combustion. Such halogenated chemical inhibitors inhibit the hydrogen combustion by interfering the chain propagating reactions of the combustion processes.

Fig. 1 shows the schematic of the hydrogen combustion studies in the presence of various chemical inhibitors. Hydrogen and air flows to the gas mixing chamber, were controlled by digital mass flow controllers. The composition of the gases was monitored by gas mixing software. A gas mixing chamber of volume  $7.5 \times 10^{-4} \text{ m}^3$  was provided with a heating jacket for vaporization and mixing of the chemical inhibitor with hydrogen-air mixture. A cylindrical type of vessel of volume  $5 \times 10^{-4} \text{ m}^3$  with spark ignition system was used for the combustion studies. Spark was generated by applying a high voltage across the tungsten electrodes with spark gap of  $5 \times 10^{-4} \text{ m}$ . A glass window of  $4 \times 10^{-2} \text{ m}$  diameter was provided on the both sides of the vessel for flame visualization by high-speed Schlieren photography. The ignition delay time was assessed by Y3-S1 Camera, 3700 fps, Nikon.

The organohalo compounds are significantly effective in hydrogen combustion inhibition and fire suppression. Ethyl bromide, dibromomethane, propyl bromide were investigated with the

hydrogen-air mixture for their inhibitory effects on hydrogen combustion. Effect of addition of various brominated hydrocarbons on the combustion of hydrogen was experimentally studied. Ethyl bromide ( $C_2H_5Br$ ), Propyl bromide ( $C_3H_7Br$ ), and Dibromomethane ( $CH_2Br_2$ ) were vaporized and individually added to the mixture of hydrogen-air mixture at 1 bar pressure. The temperature of the mixture was kept at  $10\text{ }^\circ\text{C}$  higher than the boiling point of the chemical inhibitor.

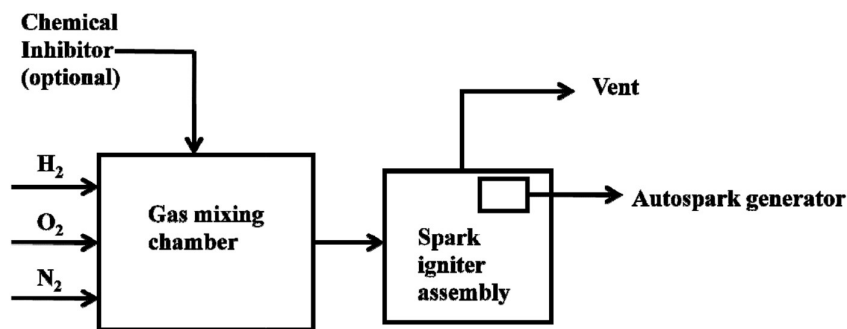


Fig. 1: Schematic of hydrogen combustion setup.

This study highlighted the flame suppression of hydrogen-air combustion in the presence of inhibitors through experimental and theoretical approaches. The experimental studies showed the impact of inhibitors on parameters like pressure elevation, the relative rate of pressure rise, delay time and burning velocity. At the same time, the sensitivity analysis, species profile and reaction path analysis theoretically supported the suppression effect.

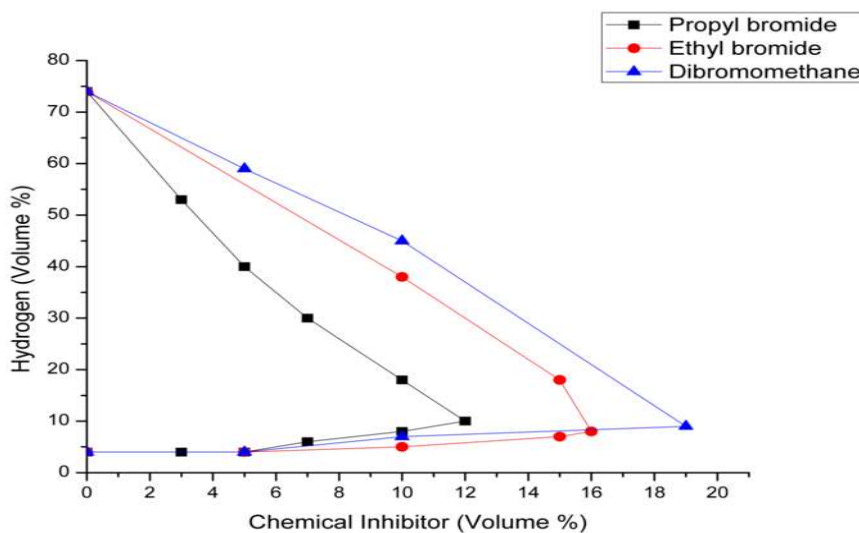
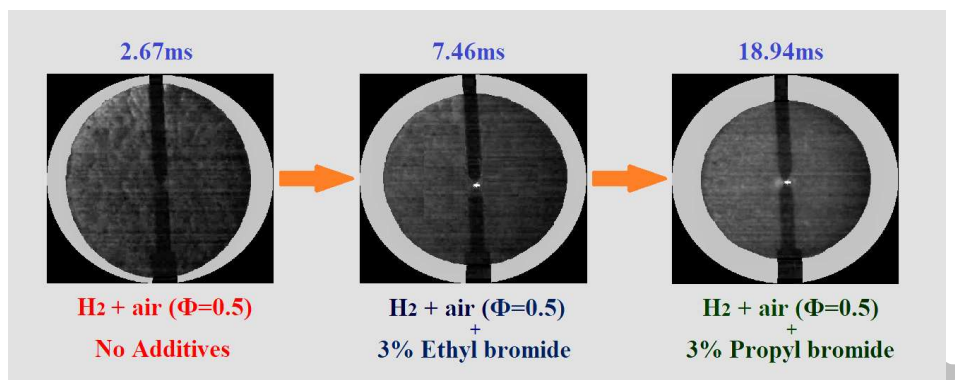


Fig. 2: Effect of chemical inhibitors on hydrogen flammability.

Significant reduction in the laminar flame speed of hydrogen-air was observed with increasing concentration of the chemical inhibitor (Fig. 2 & 3). Inhibition efficiency of these chemical inhibitors increases in the order: ethyl bromide < dibromomethane < propyl

bromide. By increasing the chemical inhibitor concentration, ignition delay time of hydrogen-air mixture also increases. Total suppression of hydrogen flammability was achieved by the addition of 12% propyl bromide, 17% ethyl bromide and 19% dibromomethane.



**Fig. 3: A typical schlieren images of hydrogen-air ( $\Phi = 0.5$ ) flames at 1 bar in presence of (a) no inhibitor, (b) 3%  $C_2H_5Br$ , and (c) 3%  $C_3H_7Br$ .**

The results demonstrate the usefulness of inhibition of hydrogen combustion by the inhibitor and their potential application in safe hydrogen handling and storage. The inhibition of hydrogen flames can be useful in reducing current challenges (hydrogen safety) in the hydrogen technology and thereby broadening the scope for smooth use of hydrogen in various usages such as transportation fuel, various industrial applications, and hydrogen fire prevention & safety for on-board applications.

#### **Sponsored Projects/ Patents/ Publications/ Thesis:**

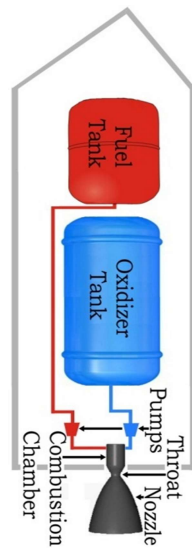
- a) Sponsored Project (2021-in progress): Development of Safe Hydrogen and its Applications, ERIPR, DRDO, Delhi (Budget: 7.4 Crores).
- b) Sponsored Project (2018): Development of non-flammable hydrogen using selected inhibitors, ARDB, DRDO, Delhi (Budget: 30 Lakhs).
- c) Sponsored Project (2016): Feasibility Studies for Development of Non-flammable Hydrogen (Phase 1), ARDB, DRDO, Delhi (Budget: 25 Lakhs).
- d) P.S. Kulkarni, S.K. Das, G.N. Joshi, Non-Flammable Lifting Gas Composition for Lighter-Than-Air Vehicle and a Method for Optimizing the Same, Patent Filed (2023).
- e) Prashant S Kulkarni, Vivekanand V. Swami, Method and Apparatus for Production of Non-flammable Hydrogen Gas, Patent No. MUM/201711034367, Patent Granted (No. 354510).
- f) Shubham K. Das; Vivekanand V. Swami; Ganpati N. Joshi; Prashant S. Kulkarni, Effect of chemical vapours on suppression of hydrogen-air explosions, Journal of Loss Prevention in the Process Industries 87 (2024) 105225.
- g) P.S. Kulkarni et al., "Effective Inhibition of Hydrogen Flames for Safe Handling and Storage" 5<sup>th</sup> Int. Conference on Advances in Energy Research 15-17 Dec. 2015 (ICAER 2015), IIT-Mumbai.
- h) Harishankar, Suppression of  $H_2$  Flammability Using various Compounds, M.Tech. Thesis (2016).
- i) V. Swami, Inhibition of Hydrogen Flames by Various Compounds, M.Tech. Thesis (2015).

## 2) Bipropellant Rocket Fuels

[Place: <sup>1</sup>Defence Institute of Advanced Technology (DU), Pune, India; <sup>2</sup>Defence Research and Development Laboratory (DRDL,DRDO), Hyderabad]

Propellants are substances or mixture of substances that do not detonate, but burn rapidly or deflagrate in a closed chamber. They are categorized into solid, liquid and hybrid propellants. Propellants undergo rapid combustion, releasing gaseous products at a rate to produce high temperature and pressure. The attained temperature and pressure provide a propulsive force to accelerate and move an object such as rockets, projectiles or missiles]. Liquid propellant is an important class of material in rocket fuel as it provides the ability to restart the mission having multiple operations and also gives the higher specific impulse (Isp) than solid propellants. There are various liquid rocket propellants: (i) monopropellants such as nitromethane, which contain both oxidizer and fuel and are ignited by some external means, (ii) bipropellants, consisting of oxidizer and fuel, which are injected into a combustion chamber from separate containers and, (iii) multipropellants, consisting of several oxidizers and fuels.

A bipropellant contains fuel and oxidizer (Fig. 4), in which, the fuel undergoes self-ignition when contacted with an oxidizer, termed as hypergolic fuel. The hypergolic fuel plays a vital role in rocket propulsion because it gives better thrust control, eliminates the external ignition source. Conventionally used fuels such as hydrazine and its derivatives (Monomethyl Hydrazine, MMH; Unsymmetrical Dimethyl Hydrazine, UDMH), are hypergolic with WFNA (White Fuming Nitric Acid), RFNA (Red Fuming Nitric Acid), and  $N_2O_4$  oxidants]. These fuels are extremely toxic, corrosive, and have high vapor pressure. Therefore, intense research is underway to develop an alternative environmentally benign, bipropellant to reduce the



**Fig. 4: A schematic of bipropellant rocket engine.**

operational costs and safety requirements associated with the handling.

Boron based compounds have been looked upon as possible replacements to conventional toxic hypergolic fuels in propellant system. In an attempt to add to the pool of boron based hypergols, a series of new amine borane/ cyanoborane zwitterionic compounds were developed (Fig. 5). Their hypergolic reactivity, performance parameters and physico-chemical properties were examined, in detail. The theoretical performance evaluation of fuels was carried out with WFNA, RFNA,  $N_2O_4$  and  $H_2O_2$  oxidizers by using the NASA-CEC-71 program. The unsymmetrical dimethyl hydrazine (UDMH) based zwitterions, UDMH-borane and UDMH-bisborane displayed strikingly lower ignition delay times of 2.2 and 2 ms, respectively (Fig. 6) and high specific impulse 241 and 245 s, respectively.

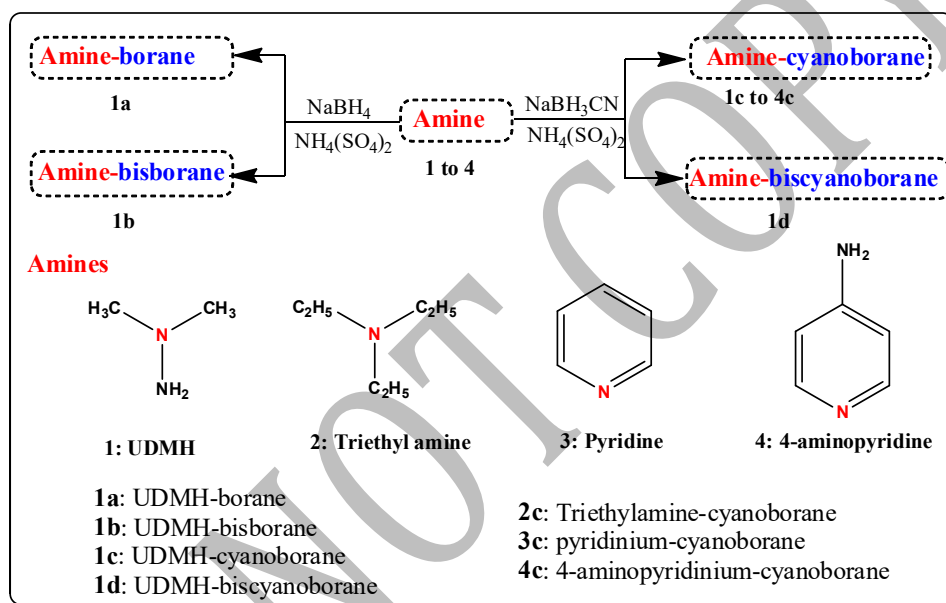


Fig. 5: Synthesis of amine-borane and amine-cyanoborane zwitterions.

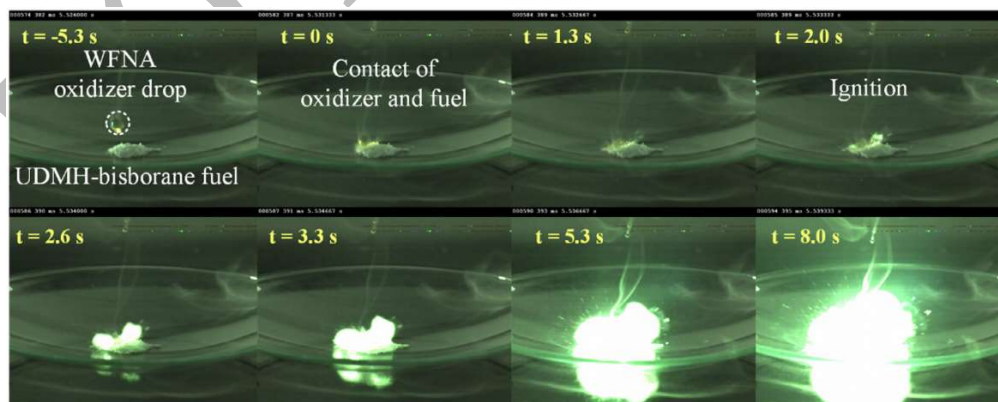


Fig. 6: A typical ignition sequence images of UDMH-bisborane fuel with WFNA oxidizer.

The pyridinium-cyanoborohydride exhibited high heat of formation (146 kJ/mol) than UDMH. While all the developed compounds exhibited higher density than the UDMH. Chemical



stability of UDMH-borane was investigated at different environmental conditions; it was found to be stable for longer duration.

In another study of hypergolic ionic liquid (HIL) development, imidazolium cations with energy-rich cyanoborohydride, [BH<sub>3</sub>CN] and dicyanamide, [DCA] anions were examined for the first time. The physico-chemical properties and performance of ILs were also studied. The analysis indicates that the IL, 1-allyl-3-octyl imidazolium cyanoborohydride is most hydrophobic and hydrolytically stable. All the ILs are liquid at room temperature and exhibit a positive heat of formation. The IL, 1,3-diallyl-imidazolium cyanoborohydride exhibited the shortest ignition delay of 1.9 ms with WFNA and IL 11, 1-allyl-3-ethyl imidazolium cyanoborohydride presented the lowest viscosity of 16.62 mPa s. Therefore, these ILs can be suggested as potential candidates for replacing acutely toxic and carcinogenic hydrazine and its methylated derivatives as hypergolic fuels

Thus, low ignition delay, good thermal and chemical stability, positive heat of formation, high specific impulse, ease of synthesis, and commercially available starting materials are the promising features of these compounds which make them attractive prospects in revolutionizing the area of green hypergolic fuel in liquid as well as hybrid rocket propulsion.

#### **Sponsored Projects/ Patents/ Publications/ Thesis:**

- a) Pilot studies (advanced) of Static Test bed conducted at DRDL, Hyderabad on selected hypergolic fuels and N<sub>2</sub>O<sub>4</sub> oxidizer (2023).
- b) Pilot studies of Static Test Bed conducted at DRDL, Hyderabad on selected hypergolic fuels and nitric acid oxidizer (2019).
- c) Sponsored Project (2012-2017): Large Scale, High Quality Nanomaterial Synthesis for Defence Applications: Coatings, Devices and Healthcare (WP4: Development of Hypergolic Ionic Liquids), ERIPR, DRDO, Delhi (Budget: 42 Crores).
- d) Prashant S Kulkarni, Shruti Soman, Vikas B. Bhosale, A Process for Preparing Hypergolic Zwitterions from UDMH and Allyl Imidazole, Patent Application No. 201811023218, Patent Granted (No. 375148).
- e) Vikas Bhosale, Studies in Ionic Liquids based Hypergolic Fuels, PhD Thesis (2017).
- f) V.K. Bhosale S.A. Karnik, P.S. Kulkarni, Ignition study of amine borane and cyanoborane based green hypergolic fuels, *Combustion and Fuels*, 210 (2019) 1.
- g) V.K. Bhosale, S.G. Kulkarni, P.S. Kulkarni, Theoretical performance evaluation of hypergolic ionic liquid fuels with storable oxidizers, *New Journal of Chemistry*, 41 (2017) 9889.
- h) V.K. Bhosale, P.S. Kulkarni, Ultrafast Igniting, Hypergolic Ionic Liquids with Enhanced Hydrophobicity, *New Journal of Chemistry*, 41 (2017) 1250.
- i) V.K. Bhosale, P.S. Kulkarni, Hypergolic behavior of Pyridinium Salts containing Cyanoborohydride & Dicyanamide Anions with Oxidizer RFNA, *Propellants, Explosives, Pyrotechnics*, 41 (2016) 1013.

### 3) Nuclear Technology

[Place: Chemical Engineering Division, Bhabha Atomic Research centre, Mumbai, India]

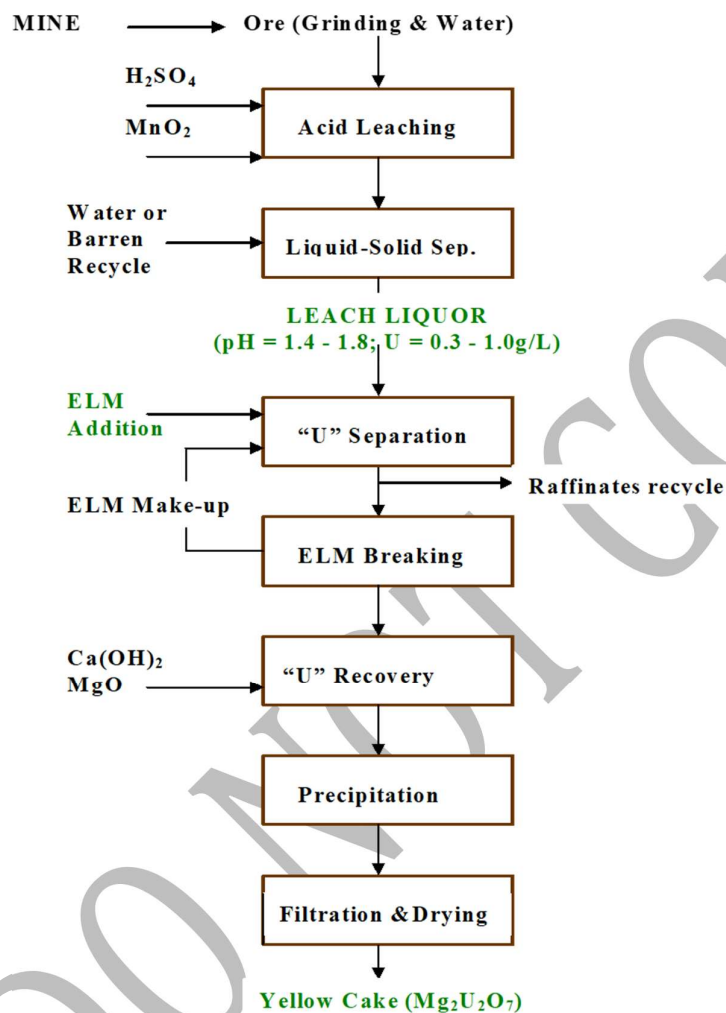
**Recovery of uranium from leach liquor:** A uranium metal production plant in India is located at Jaduguda, Singhbhum Shear Zone, Bihar. The ore consists of quartz, chlorite, and sericite, with negligible amounts of apatite and magnetite, having a uranium concentration ranging from 0.06% to 0.07%  $U_3O_8$ . Uraninite is the major uranium-bearing mineral, and uranium is extracted by leaching with sulfuric acid using pyrolusite as an oxidant. The uranium material is recovered by solvent extraction and/or ion exchange and eventually precipitated as a yellow cake of magnesium diuranate ( $MgU_2O_7$ ).

Although these conventional separation processes have been in use for many years, they suffer from limitations; for example, the solvent extraction process includes the need for dispersion and coalescence, problems of emulsification, the requirement of more steps, flooding and loading limits in continuous counter current devices, the need for density differences between the phases, phase disengagement difficulties, use of a scrubber, high solvent losses, and large solvent inventories. The ion exchange process suffers from the problem of resin fouling, capacity limitations, the requirement of more complexing material, and selectivity. Moreover, these separation processes are equilibrium-limited. In view of this, a new, emulsion liquid membrane (ELM/LEM) technique was proposed.

The ELM/LEM technology refers to simultaneous extraction and stripping, where metallic solutes present in lean solution form a complex with the extractant. The complex formed then diffuses through a membrane phase to a stripping phase interface from where it is stripped into the bulk of encapsulated stripping phase. The volume of stripping zone liquid is very small compared to aqueous feed phase, thereby resulting in concentration of uranium. The concentrated uranium from the strip phase can be recovered by breaking the emulsion.

Therefore, the application of the ELM technique was tested for the efficient recovery of uranium from the leach liquor, in the presence of metal ions such as Fe, Ca, Mg, and Mn. The liquid membrane employed consisted of a diluent (light and heavy paraffin), a surfactant (Span 80), and an extractant (Alamine 336), and sodium carbonate was used as the stripping solution. Initially, the ELM process parameters were optimized by using synthetic leach liquor as the feed phase. The role of the acidic feed-phase pH, which enhances the cotransport of  $H^+$  ions along with uranium inside the emulsion globules, was found to be significant, as it helped in achieving the complete extraction and stripping of uranium. The best optimized parameters were directly used for the separation and concentration of uranium from industrial leach solutions. In one step, in the presence of various metal ions, the selective permeation of uranyl ions through the liquid membrane was observed to be

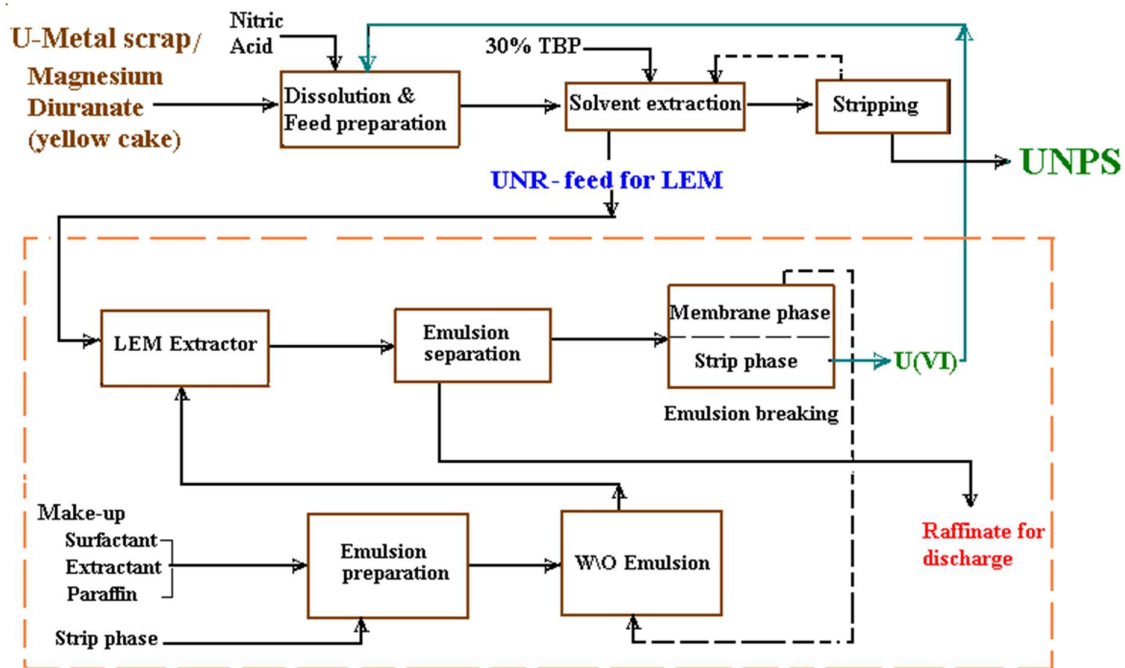
greater than 90%, and the concentration of uranium inside the strip phase was observed to be nearly 7 times higher. Separation factors of uranium with respect to Fe, Mg, Ca, and Mn were experimentally found to be 129, 781, 43, and 1462, respectively, in 12 min. Finally, application of the process in uranium ore processing is demonstrated (Fig. 7).



**Fig. 7: Proposed ELM -based scheme for the separation and concentration of uranium from leach liquor of Jadugoda ore.**

**Recovery of uranium from acidic waste:** Acidic wastes containing low concentrations of uranium are generated during uranium purification and processing (UNR). This study has been initiated to develop a suitable ELM technique for selective separation and recovery of uranium from such wastes using tri-n-octylphosphine oxide (TOPO) in paraffin as a carrier and sodium carbonate as a stripping agent. The waste, having a composition of nearly 600 ppm U(VI), 360 ppm Fe(III), 325 ppm Ca(II), 390 ppm Mg(II) at an acidity of 1.2 M  $HNO_3$ , was used as the feed phase (Fig. 8). Various factors that affect the emulsion stability as well

as percentage extraction of uranium have been optimized in order to obtain maximum concentration of uranium from acidic wastes. An attempt was made to recover uranium without making any substantial changes to the wastes composition. In presence of various metal ions, selective permeation of uranyl ions through liquid membrane was observed to be more than 70%. Batch type extractions of U(VI) by the ELM method were performed to simulate a two-stage counter extraction and the experimental findings suggest that the U(VI) concentration in the final raffinate can be lowered to below 50 ppm. Potential of the method for the selective separation of U(VI) from acidic wastes is, established.



**Fig. 8: Proposed ELM -based scheme for the separation and concentration of uranium from acidic waste.**

**Sponsored Projects/ Patents/ Publications/ Thesis:**

- Pilot plant studies on recovery of uranium from leach liquor of Jdugoda ore, at Chemical Eng. Division, BARC, Mumbai (2002).
- P.S. Kulkarni, "Recovery of Uranium (VI) from Acidic Wastes Using Tri-n-octylphosphine Oxide and Sodium Carbonate Based Liquid Membranes", *Chemical Engineering Journal*, 92 (2003) 209. (Single Author)
- P.S. Kulkarni, et al. "Studies on Membrane Stability and Recovery of Uranium (VI) from Aqueous Solutions Using a Liquid Emulsion Membrane (LEM) Process", *Hydrometallurgy*, 64 (2002) 49.
- P.S. Kulkarni, et al. "The Liquid Membrane Process for the Selective Recovery of Uranium from Industrial Leach Solutions" *Industrial & Engineering Chemistry Research*, 48 (2009) 3118.

#### 4) Biofuels and Applications

[Place: <sup>1</sup>Centre for Green Chemical Processes, New University of Lisbon, Lisbon, Portugal;  
<sup>2</sup>Defence Institute of Advanced Technology (DU), Pune, India]

**Selective extraction of biofuel (limonene) from orange peels by organophilic pervaporation:** Pervaporation is a membrane separation technique, whose separation principle is based on the preferential partitioning of a solute from a liquid feed phase into a dense, non-porous membrane through which it diffuses according to its chemical potential gradient. This gradient is the driving force for the solute transport across the membrane. It is in general established by maintaining a low vacuum on the membrane downstream side, while keeping the membrane upstream side, which is in contact with the liquid feed, under mild conditions, at ambient pressure. According to the solution–diffusion model, the partial flux  $J_i$  of a solute  $i$  across the membrane is given:

$$J_i = \frac{S_i \cdot D_i}{Z_m} \cdot \Delta\mu_i = \frac{S_i \cdot D_i}{Z_m} \cdot (\mu_i^f - \mu_i^p)$$

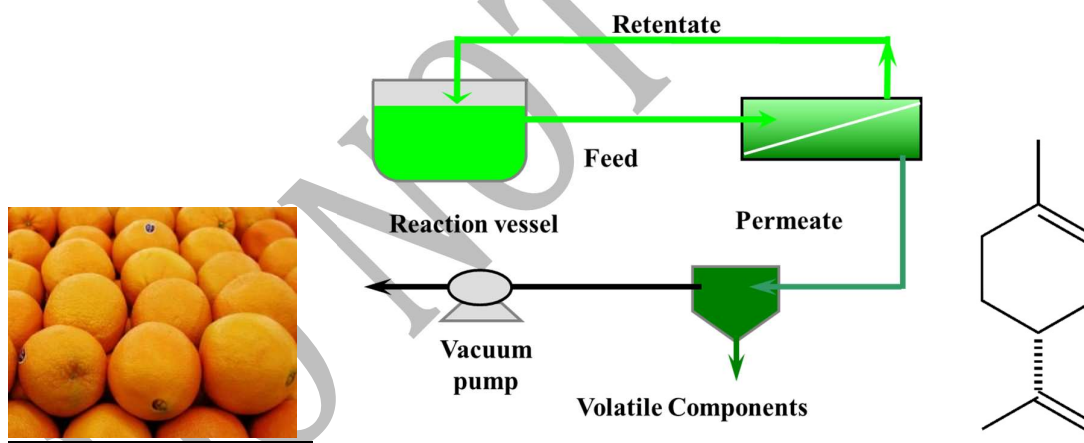
with  $S_i$  the sorption coefficient of solute  $i$  between the feed liquid phase and the membrane;  $D_i$  the diffusion coefficient of  $i$  in the membrane;  $z_m$  the membrane thickness; the chemical potential gradient of  $i$  over the membrane in the liquid feed phase and the permeate, respectively. By selecting the right type of membrane, it is possible to control which compound will preferentially remain in the feed and which will preferentially permeate through.

The potential advantages of the use of benign solvents with extremely low vapour pressure for recovery of target solutes by pervaporation can be summarized as: i) benign solvents can solubilise a large range of organic molecules, that may present reduced solubility in conventional solvents; ii) due to their non-measurable vapour pressure, benign solvents with extremely low vapour pressure, unlike water and aqueous-based solvent systems, do not desorb to the vapour phase at the downstream surface of non-porous, dense membranes, whether they are organophilic or hydrophilic, which allows for solute recovery free of solvent, under the operating conditions used; recovered solutes do not get contaminated by the solvent and therefore do not need further purification for solvent removal; iii) there are no solvent losses from the original feed neither to the permeate nor to the environment, which reflects on the process economy and environmental benignity; and hence the solvent can be reused; iv) due to selective solute– polymer interactions, it is possible to remove/recover target solutes from the reaction media, while keeping other products; solute recovery may be governed by these interactions.

Our case-study is, to a recover D-limonene (biofuel) from the orange peels by using pervaporation process. the orange peels contain more than 40 compounds, with high

amounts of different important monoterpenes, mainly limonene. Due to its high solvency, attractive citrus odour and versatility, D-limonene is also used in wide range of products and applications, such as a flavouring or fragrance in the food and cosmetic industry, or as a solvent in household and industrial cleaner.

In this work, an integrated and sustainable process is proposed consisting of using benign solvents for the extraction of target compounds, followed by organophilic pervaporation for their recovery and fractionation (Fig. 9). Indeed, limonene is a high value product obtained from a source that is mostly disposed. The effect of different benign solvents in this sustainable process is studied, and organophilic pervaporation is compared with the traditional vacuum distillation in terms of global efficiency of the process. The integration of the process was succeeded. Alimentary oil and polypropylene glycol 240 efficiently solubilised limonene, the target compound in this work. Furthermore, organophilic pervaporation enabled an efficient concentration of limonene, with fewer contaminants, and it also enabled a lower water content when compared with the traditional vacuum distillation, which favours the stabilisation of the target solute. The combined extraction-pervaporation process has thus shown great potential in selective recovery of biofuel, limonene from the orange peels.

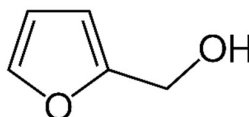


**Fig. 9: a) Orange peels, b) Schematic of Pervaporation process, and c) Structure of limonene (biofuel).**

### **Ionic Liquid and Biofuel Blend: A Low-cost Hypergolic Fuel for Propulsion**

**Application:** In the present study, we reported a new fuel blend of hypergolic ionic liquid, HIL, 1-ethyl-3-methyl imidazolium cyanoborohydride [EMIM] [BH<sub>3</sub>CN] and a biofuel, furfuryl alcohol (Fig. 10) in different volume proportions (80:20, 70:30, 60:40, 50:50 & 40:60) as promising liquid fuels for rocket application. It exhibits hypergolic ignition with known storable oxidizers. The proven HIL, [EMIM][BH<sub>3</sub>CN] exhibits low ID, good thermal stability, liquidous over wide temperature range and obtained in high yield (> 95%). In order to increase the

density, lower the viscosity and reduce the cost of HIL, it was blended with biofuel, furfuryl alcohol in different volume proportions. Furfuryl alcohol has been selected for the purpose because it is manufactured by catalytic reduction of furfural which is an agro product, obtained from biomass such as rice husk and sugarcane (pentose sugar). Therefore, it is an environmentally and eco-friendly ingredient, easily available in the open market with reasonable cost. It had low viscosity (5 mPa·s), high density (1.134 g/cm<sup>3</sup>), low vapor pressure (0.5 mmHg at 20 °C) and good thermal stability (B.P. 170 °C).



**Fig. 10: Structure of Furfuryl alcohol**

The hypergolic fuel, [EMIM][BH<sub>3</sub>CN]: furfuryl alcohol blends reported in the current investigation appears to be very promising in terms of the physical parameters like density, viscosity, thermal stability; the combustion parameters like ignition delay, the heat of combustion and performance parameters like specific impulse and density specific impulse. In addition to this, the HIL, [EMIM][BH<sub>3</sub>CN] is easy to synthesize in high yield which exhibits hypergolic shortest ID and good thermal stability ( $T_d = 221$  °C). Furfuryl alcohol which is used as biofuel in the present study to form the blends with HIL is a renewable product having high density and low freezing point. Overall, the blends exhibit good stability, low viscosity (< 15 mPa·s), high density (> 1 g/cm<sup>3</sup>), low ignition delay and high performance in comparison with UDMH - a proven liquid fuel presently being used as promising fuels for liquid rocket application. The reported blends appear to be a technologically promising, eco-friendly and affordable fuel blend to replace currently used liquid toxic fuels.

#### **Sponsored Projects/ Patents/ Publications/ Thesis:**

- a) P.S. Kulkarni, et al. "Selective extraction of natural products with benign solvents and recovery by organophilic pervaporation: fractionation of D-limonene from orange peels", *Green Chemistry*, 12 (2010) 1990.
- b) V.K. Bhosale, S.G. Kulkarni, P.S. Kulkarni, Ionic Liquid and Biofuel Blend: A Low-cost and High Performance Hypergolic Fuel for Propulsion Applications, *Chemistry Select*, 1 (2016) 1921.

## 5) Solar Energy Materials

[Place: Defence Institute of Advanced Technolgy (DU), Ministry of Defence, Pune, India]

With rapidly expanding economies and growing population, the need for energy around the globe is also heading upwards. To counter these demands, the focus of research has shifted to large-scale development of renewable sources of energy. Thermal energy storage (TES) or solar energy storage materials can effectively be used to bridge the gap by minimizing the energy requirement. It can be captured through sensible heat storage, latent heat storage by using phase change materials (PCMs), thermochemical reactions, adsorption and absorption storage. Latent TES offers high energy storage density under isothermal conditions compared to sensible heat storage technology and can offset the current growing demands of energy management and conservation. PCMs use latent heat to store energy, allowing heat storage and release during phase transformation. For a material to be used effectively as a PCM, it should meet criteria such as large phase change enthalpy, cyclic stability, good thermal conductivity, minimum expansion/contraction during phase change, chemical stability and low costs. PCMs function by absorbing energy during the fusion process with the collapse of the crystalline solid structure. While cooling down during the crystallization process, energy is released back into the surroundings. This makes the system unique as regeneration is taken care of by the surroundings during the idle period and the system becomes maintenance free. The entire system is depicted in Fig. 11.

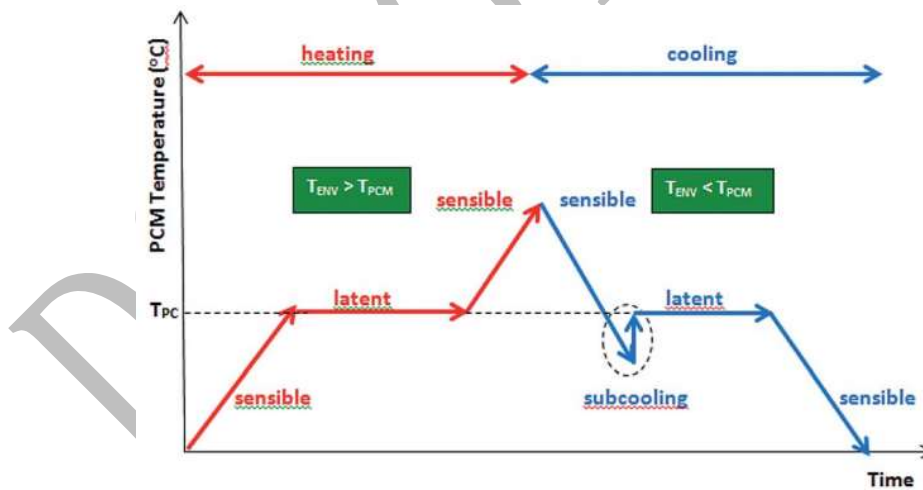


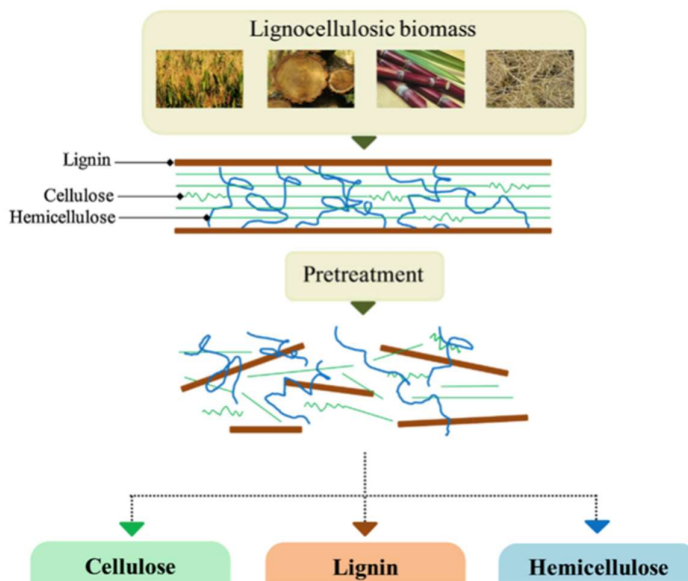
Fig. 11: Schematic representation of a working PCM or solar energy storage materials.

PCMs can be segregated based on the phase change state as solid–solid, solid–liquid and liquid–gas. Solid–solid phase transition has gained importance due to its independency for designing of separate storage containers and its stability over the wide temperature range without liquid leakage. PCM involving solid–solid phase change is commonly called as form–stable or shape–stabilized PCM (SSPCM). They can be prepared by using physical or



chemical methods. The SSPCMs using physical methods, are formed by dispersing PCMs (soft segment) into higher melting point polymer (hard segment) which act as porous matrix or supporting material. With increase in temperature, the solid-liquid PCM entrapped in the polymer matrix undergoes phase transformation. But, due to presence of this supporting material, it retains its shape and undergoes a crystalline to amorphous phase transition.

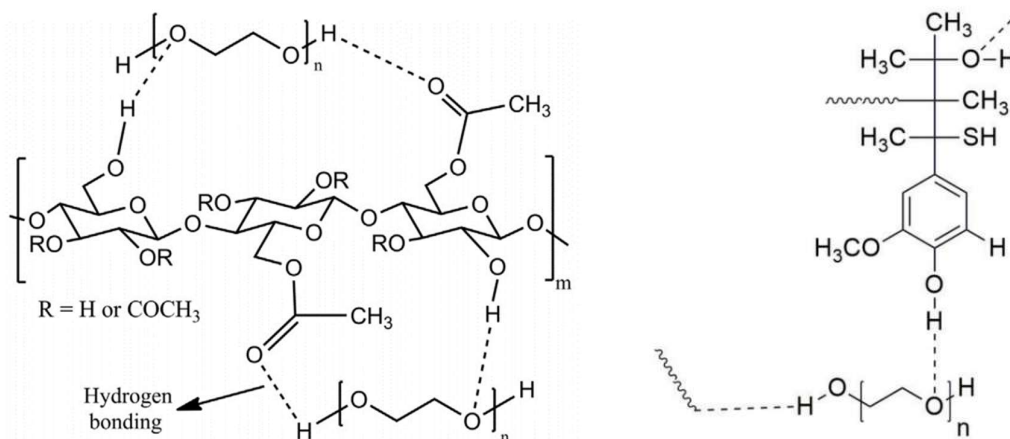
Cellulose and lignin are the most abundant naturally occurring polymer obtained from biomass (Fig. 12). Therefore, both have been explored as a hard segment material while polyethylene glycol has been used as soft segment material.



**Fig. 12: Lignocellulosic biomass.**

Microwave technology-based process development for the preparation of form stable phase change composites was attempted, with the motivation of establishing a green technique, which will be energy and time efficient and require minimum amount of solvent. The process could easily be scaled for large scale production of PCM blends. The microwave-assisted blending of PEG and cellulose acetate (CA) was carried out in various ratios resulting in the formation of biodegradable form-stable PCM (Fig. 13a). PEG acted as the latent heat storage material and cellulose acetate as the supporting material. As a result of microwave treatment, a high loading capacity of 96.5 wt% PEG was achieved without any leakage during the transition process. The blending was confirmed by Fourier transform infrared spectroscopy (FTIR) analysis which showed no chemical bonds between PEG and CA. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) indicated that maximum enthalpy of 155 J/g was attained and the material was found to have good thermal stability. The X-ray diffraction (XRD) investigation revealed that the crystallinity of the PEG-CA blend increased with increasing concentration of PEG. The morphology was studied with

field-emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) suggesting a homogeneous network formation of the blend.



**Fig. 13: a) PEG-CA and b) PEG-Lignin form stable energy storage material.**

In other case, lignin, an abundant bioresource and a natural polymer, is investigated for its use as the supporting material while poly(ethylene glycol) (PEG) has been used as the working element (Fig. 13b). Various ratios of PEG and lignin were studied and the shape-stabilized phase change material (SSPCM) was prepared using microwave assisted blending, which proves to be one of the efficient and green ways of preparing the blends. The thermal and crystalline properties were investigated using differential scanning calorimetry, thermogravimetric analysis and X-ray diffraction. The morphology was studied with field-emission scanning electron microscopy (FESEM), energy dispersive X ray spectroscopy (EDAX) and polarized optical microscopy (POM) suggesting a homogeneous network formation of the composite. Maximum loading of PEG was found to be 70%, giving enthalpy of 100.91 J/g. The prepared PCM exhibited excellent thermal reliability even after 100 thermal cycles. This novel PCM blend of PEG and lignin is considered as a promising candidate in terms of reliability and renewability making it suitable for various thermal energy storage applications.

This energy can be tapped and utilized in various sectors such as building applications, textile industry, smart packaging, solar energy storage, temperature adaptable greenhouses, cooling of electronic circuitry, waste heat recovery and many more emerging areas

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- c) M. Deshpande, S. Sundararajan, A.B. Samui, P.S. Kulkarni, Microwave Assisted Preparation of Poly(ethylene glycol)/Lignin Blends for Thermal Energy Storage, *Journal of Energy Storage* 35 (2021) 102338.
- d) S. Swati, A.B. Samui, P.S. Kulkarni, Shape-stabilized PEG-cellulose acetate blend preparation with superior PEG loading via microwave-assisted blending, *Solar Energy*, 144 (2017) 32.
- e) S. Swati, A.B. Samui, P.S. Kulkarni, "Interpenetrating Phase Change Polymer Networks Based On Crosslinked Polyethylene Glycol And Poly(Hydroxyethyl Methacrylate)", *Solar Energy Materials and Solar Cells*, 149 (2016) 266.
- f) S. Swati, A.B. Samui, P.S. Kulkarni, Crosslinked polymer networks of poly(ethylene glycol) (PEG) and hydroxyl terminated poly(dimethyl siloxane) (HTPDMS) as polymeric phase change material for thermal energy storage, *Solar Energy*, 181 (2019) 187.
- g) S. Swati, A.B. Samui, P.S. Kulkarni, Synthesis and characterization of poly(ethylene glycol) acrylate (PEGA) copolymers for application as polymeric phase change materials (PCM), *Reactive and Functional Polymers*, 130 (2018) 43.
- h) S. Swati, A. Kumar, B.C. Chakraborty, A.B. Samui, P.S. Kulkarni, Poly(ethylene glycol) (PEG) modified epoxy phase change polymer with dual properties of thermal storage and vibration damping, *Sustainable Energy & Fuels*, 2 (2018) 688.
- i) S. Swati, A.B. Samui, P.S. Kulkarni, Thermal energy storage using poly(ethylene glycol) (PEG) incorporated hyperbranched polyurethane as solid-solid phase change material (PCM), *Industrial & Engineering Chemistry Research*, 56 (49) (2017) 14401.
- j) A. Kumar, P.S. Kulkarni, A. B. Samui, "Polyethylene glycol grafted cotton as phase change polymer", *Cellulose*, 21(1) (2014) 685.
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## 6) Waste to Energy

[Place: <sup>1</sup> Italian National Agency for New Technologies, Energy & Sustainable Development (ENEA), Rome, Italy; <sup>2</sup>High Energy Materials Research Laboratory (HEMRL, DRDO), Pune, India; <sup>3</sup>Defence Institute of Advanced Technology (DU), Pune, India]

### 1) Fertilizers from Life-Expired Propellants

During the manufacture of nitramine propellant (NP) and fuel-rich-based propellant (FRP), lot of waste is accumulated due to rejection of lots and also their expiry of service life. The accumulation of such stores causes fire hazards; therefore, demilitarization of surplus and rejected stores has been a requirement over the years. At present, the primary means of demilitarization/disposal of these stores are by open burning/open detonation (OB/OD); however, this method of disposal is not acceptable because of the risk involved to human health and toxicity to the environment. Therefore, it was thought to develop a safer method of conversion of NP and fuel-rich-based propellant into fertilizer.

A systematic study has been carried out to convert waste/rejected NP and fuel-rich-based propellant FRP into liquid fertilizer by digesting in dilute nitric acid followed by neutralization with potassium hydroxide and phosphoric acid (Fig. 14). The obtained liquid fertilizers were

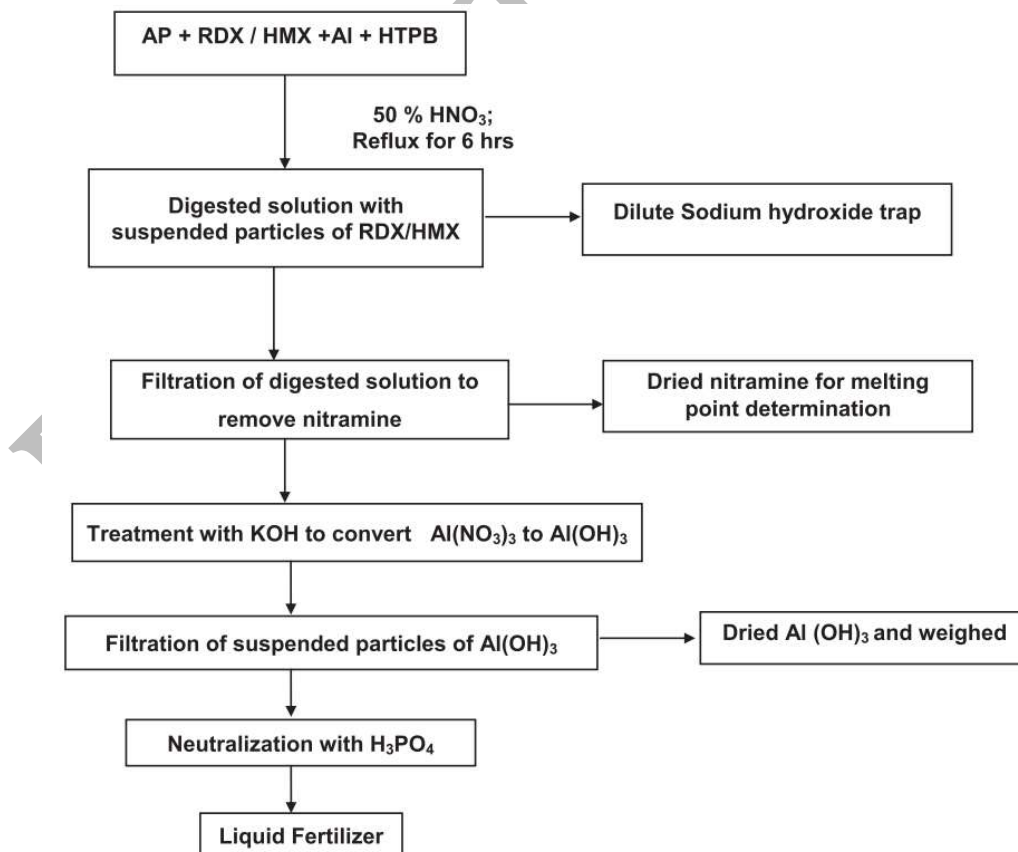


Fig. 14: Flow diagram for conversion of NP into liquid fertilizer

fully characterized for nitrate, phosphate and ammonium ions along with potassium. Further, the effect of liquid fertilizers of NP and FRP on cluster bean plants was studied by taking different concentrations and their effects on germination pattern, shoot growth, thickness of stem, size and number of leaves, number of pods and length over a full-grown period of plants were investigated. The results reveal that the germination index increases as the content of liquid fertilizer increases and the same trend was observed with respect to root and shoot growth. Also, broadness and the number of leaves showed an encouraging effect as concentration increases.

**Research Output:**

- a) S. Anu Abirami, Development of an Eco-friendly Method to Convert Life Expired Fuel Rich Propellant, Ph.D. Thesis 2019.
- b) S. Anu Abirami, K. Dhabbe, P.S. Kulkarni, Mehilal, Studies on conversion of waste nitramine and fuel rich based propellants into liquid fertilizer and their performance on crop, *Environmental Technology*, 40 (8) (2019), 1035.

**2) Extraction of high energy materials from waste**

Extraction using ionic liquids: The contamination of energetic materials in wastewater during its production and application is one of the serious environmental issues. Selected hydrophobic ionic liquids (ILs) were developed, characterized and applied for the separation of EMs such as TNT, tetryl and picric acid from aqueous medium. Batch-wise extraction experiments were performed at 700 rpm in a capped glass vial at 25 °C (Fig. 15). The IL containing anion, bis(trifluoromethanesulfonyl)imide ([NTf<sub>2</sub>]) played a vital role in the separation of EMs due to its large ionic radius. It was, therefore, extensively used for the optimization of various process parameters. The investigation of the extraction mechanism has revealed that a C–H- $\pi$  interaction is present between the IL and EM. The results show the highest distribution ratio of 2095 for the tetryl amongst the other EMs used. A maximum separation factor for tetryl/TNT, TNT/picric acid and picric acid/tetryl was observed to be 1.75, 6.65 and 0.15, respectively for the IL, 1-octyl-3-methylimidazolium bis [trifluoromethanesulfonyl] imide ([OMIM][NTf<sub>2</sub>]). After the extraction, the IL was separated from the aqueous phase and repeatedly treated five times with a fresh batch of EM.

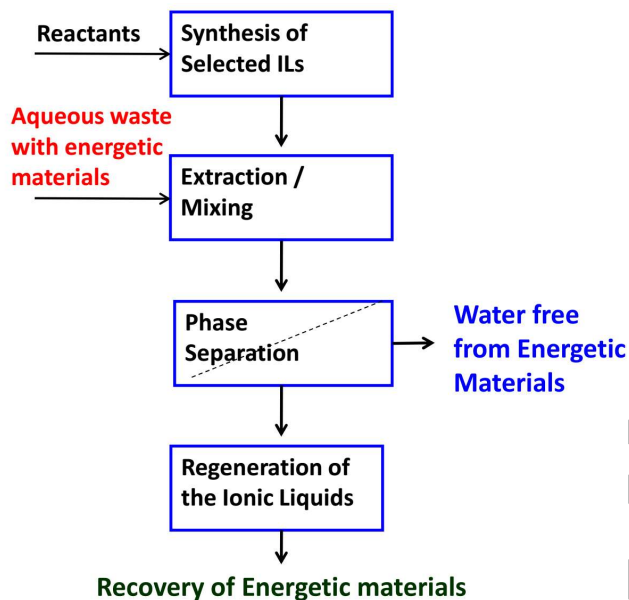


Fig. 15: Extraction of energetic materials using ionic liquid.

Extraction using supported ionic liquid membranes (SILM): The present investigation deals with separation of various types of nitrophenols using SILM technique. Several ionic liquids were developed and the SILM parameters such as role of ILs, feed and strip phase concentration, wastewater pH, salt effect and mixture of pollutants were thoroughly investigated. The percentage extraction and stripping, flux, apparent rate constants and selectivity were evaluated. The selected ammonium IL being more polar than the imidazolium IL showed better separation of 2-nitrophenol. The SILM constituting an ammonium IL with SCN anion exhibited extraction efficiency of >96% and  $K_a$ :  $0.264 \text{ h}^{-1}$ . The change in feed concentration showed maximum transport of nitrophenol at 300 ppm concentration ( $K_a$ :  $0.673 \text{ h}^{-1}$ ). The membranes were repeated for 4 cycles which demonstrated good stability for runs of more than 48 hours. The selectivity of 2-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol over nitrobenzene was 26, 36 and 58, respectively. The morphology of membranes was studied by using FTIR and FE-SEM and the transport mechanism was elucidated (Fig. 16). With the optimized parameters, a concentration factor of 7 can be achieved in the present SILM system. The application of SILM including ammonium IL with SCN anion shows a promising potential for the recovery TNT from aqueous waste.

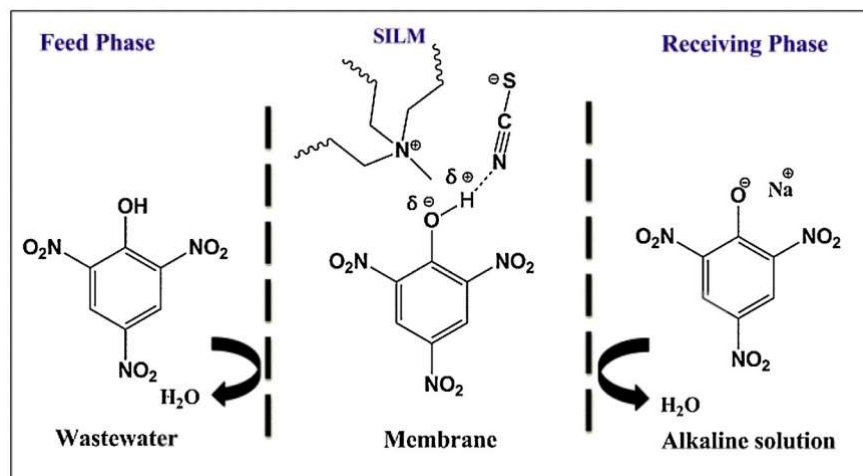


Fig. 16: Mechanism of transport of TNT inside SILM.

#### Sponsored Projects/ Patents/ Publications/ Thesis:

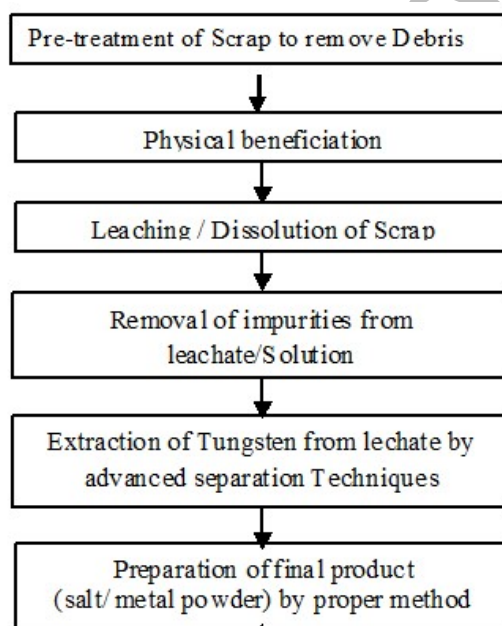
- Prashant S Kulkarni, Vikas B. Bhosale, Extraction and recovery of energetic materials using ionic liquids, Patent No. 2731/MUM/2013, Patent Granted (No. 337928).
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- V.K. Bhosale, H.K. Chana, S.P. Kamble, P.S. Kulkarni, Separation of nitroaromatics from wastewater by using supported ionic liquid membranes, *Journal of Water Process Engineering*, 32 (2019) 100925.
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### 3) Efficient reclamation of precious metals

Recovery tungsten from industrial scrap: There are several reasons for recycling tungsten scrap. First, most scrap materials are richer in tungsten than ore concentrations, making tungsten scrap a worthy material for recycling. Second, the demand for tungsten products is increasing; consequently, the demand for tungsten resources is rising. Companies can lower their raw material costs and make greater profits by recycling tungsten scrap. Third, recycling tungsten scrap has many environmental benefits, such as reducing land-filled waste, saving valuable and finite virgin raw materials and energy, as well as reducing pollution. The production of tungsten is of meagre quantities in comparison to its demand of approximately 2000 tonnes/year. In order to lessen the burden and supply to the country's defence programmes, India is required to focus on various available secondary and lean grade sources such as scrap and tailings.

The methodology opted is a combination of pyro and hydro metallurgical techniques, which can be termed as "Combinational (Pyro + Hydro) metallurgical reclamation". In this

process the industrial heavy metal scrap of tungsten will be initially heat treated which is a pyro operation, preceded by removal of debris by pre-treatment which involves washing with a suitable solvent and dried. Then obtained product, scrap oxide is subjected to physical beneficiation to accomplish ease of handling and treatment. Then the scrap oxide powder is dissolved or leached with a suitable solution. The impurities present in the resulting leachate/solution will be removed by employing the suitable methods and further subjected to advanced techniques of separation to extract or recover the tungsten. Then the value added form of the tungsten i.e., salt/metal powder is prepared by precipitation or reduction. Further the process parameters and results of bench mark studies will be validated and optimised to develop a final schematic design for the reclamation of tungsten which is an industrially viable cost-effective solution. The Scheme is represented in flowchart shown below (Fig. 17).



**Fig. 17: Schematic for the recovery of tungsten from industrial scrap.**

Recovery titanium from municipal solid waste fly ash: The incineration of municipal solid wastes produces several volatile heavy metals and these metals are vaporized as chlorides and concentrated in newly formed fly ash (FA) due to the application of the air control system to reduce the emissions of contaminants to the atmosphere. The FA produced during the incineration process is appreciatively within 10-30 kg of dry matter per ton of refuse. The FA contains many elements such as titanium that could be recovered instead disposed as hazardous waste. This investigation has shown that sulphuric acid leaching of fly ashes is effective where most of Ti was dissolved, then a selective recovery by solvent extraction is indispensable to obtain pure compounds. We have demonstrated that hydrometallurgical



treatment of FA to recover some materials and in particular quaternary titanium is a potentially feasible method.

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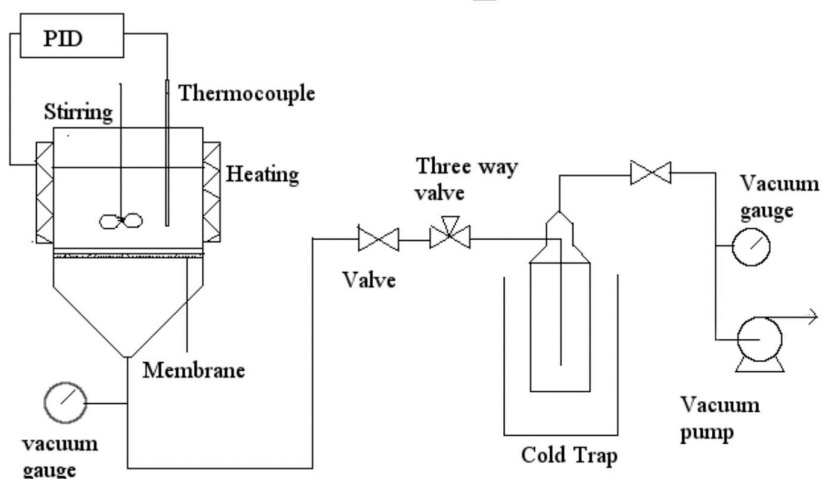
#### **4) Dehydration of Hydrazine Hydrate by Pervaporation Process**

Hydrazine is used as a liquid propellant in rocket engines and monopropellant in satellites. It also has many industrial applications. Hydrazine is manufactured by different processes. Hydrazine is obtained in the form of its solution in water. It is known as hydrazine hydrate. Commercially available hydrazine hydrate has 64 % w/w hydrazine in water. However, for space applications, hydrazine of high purity is required. This makes it necessary to separate hydrazine and water.

Hydrazine and water mixture shows a phenomenon called azeotrope. An azeotrope is a mixture of two liquids which shows a constant boiling point and composition throughout distillation. This makes it impossible to separate the components using conventional distillation methods. Hydrazine is separated using a method called azeotropic distillation. In azeotropic distillation, a third component is added in the mixture which is able to generate another azeotrope with either hydrazine or water, thereby removing that component from the mixture. This is a complicated process and involving much higher initial investment than conventional distillation. The explosive nature of hydrazine further complicates the process.

All these factors contribute to the cost difference between hydrazine hydrate and pure hydrazine. pervaporation can be an excellent alternative in case of hydrazine because it is not affected by azeotrope and it can offer much higher separation factor per stage than conventional method. There is a possibility of reducing the cost of pure hydrazine by application of pervaporation. The objectives of present work includes: a) Selecting a new membrane material for this application, b) Finding a suitable membrane preparation method for new material, c) Preparing the membrane and performing the experiments with it to study its performance characteristics.

In this regard, PMMA is selected as a membrane material for this application. The membranes of PMMA are prepared and tested for their selectivity and flux. Effects of concentration and membrane thickness on the flux and selectivity are studied (Fig. 18). PMMA shows no signs of degradation in presence of hydrazine and shows moderate flux and selectivity for water in case of this application. Performance of the PMMA is improved by addition of zeolite 13X as hydrophilic fillers. Significant change in performance of the membrane after incorporation of zeolite 13X.



**Fig. 18: Experimental setup of pervaporation.**

**Sponsored Projects/ Patents/ Publications/ Thesis:**

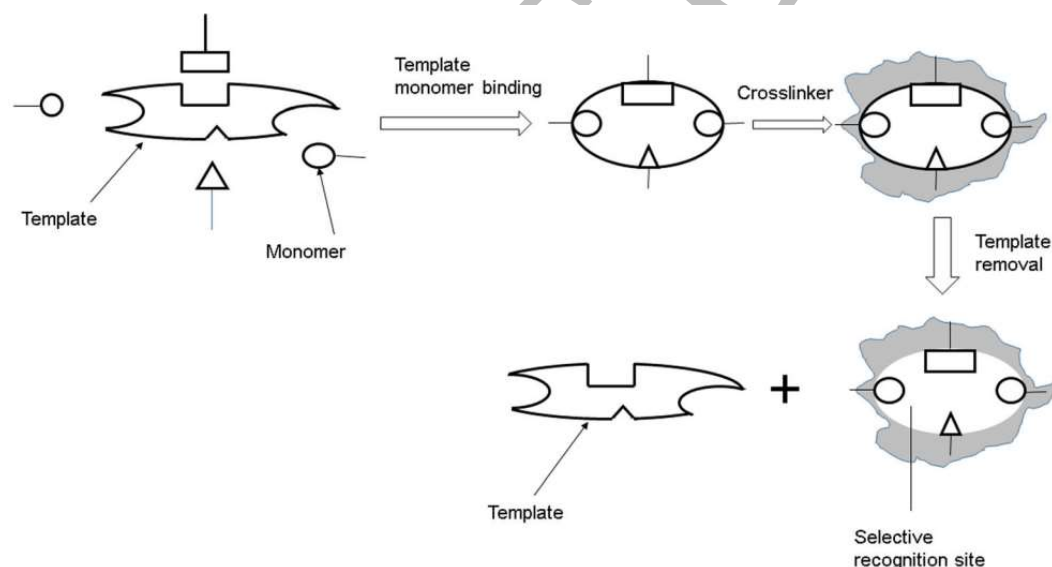
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## ENVIRONMENTAL RESEARCH

### 1) Sensing & removal of pollutants using MIPs

[Place: Defence Institute of Advanced Technology (DU), Ministry of Defence, Pune, India]

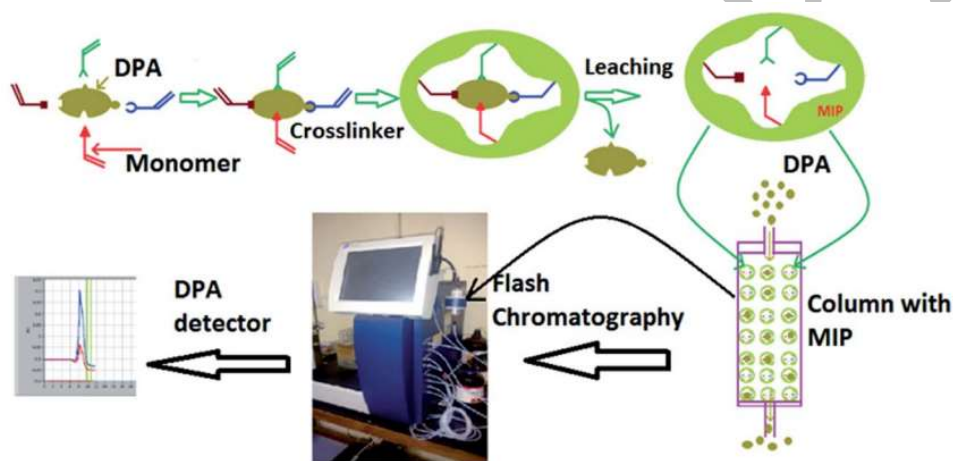
Selective separation/ extraction of pollutants or target compounds and its recovery can be easily achieved by using molecularly imprinted polymer technology (MIP). MIP is a technology used to create recognition sites in macromolecular matrix using a template molecule. The processes involved in the development of MIP are shown in Fig. 19. Basically, MIP is the development of the key-and-lock model. Ion-imprinted polymer is synthesised by using template (pollutant/ target), monomer, crosslinker and initiator. After the formation of polymer, pollutant or target compound is extracted and cavities are created for specific metal ions. This imprinted polymer is used for selective extraction of organics or metal ions. MIPs are different from ion imprinted polymers (IIPs) in case of template. In IIPs, metal ions are templates while in MIPs, molecules are templates. There are two approaches in imprinting technology, a covalent and non-covalent or self-assembly. Due to these approaches broad range of applications are possible using these techniques.



**Fig. 19: Process involved in the development of MIP or IIPs.**

One of the aims of the study was to prepare MIP for the selective recognition of diphenyl amine (DPA: used as stabilizer in propellant) and its combination with flash column chromatography for the continuous extraction of DPA from ammunition waste (Fig. 20). The DPA-MIP was prepared by free radical polymerization using methacrylic acid as a complexing monomer and EGDMA as a crosslinker. Methanol and acetic acid (9:1) were used as a leaching agent for DPA. MIP showed maximum adsorption capacity at pH 4. The

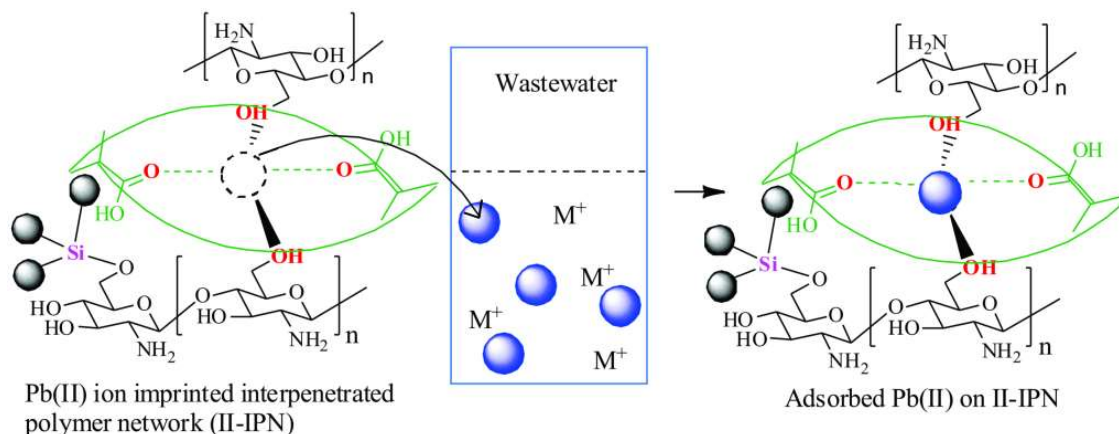
maximum experimental adsorption capacity obtained for MIP and NIP (non imprinted) particles were  $31 \text{ mg g}^{-1}$  and  $10.2 \text{ mg g}^{-1}$ , respectively. Langmuir and Freundlich adsorption isotherm models were used to analyze the experimental data of DPA adsorption on MIP. The Freundlich adsorption isotherm model fit very well with this. Pseudo first order and pseudo second order kinetic models were used to estimate the corresponding rate parameters, equilibrium capacities and correlation coefficients. The selectivity coefficients of MIP for DPA in the presence of NDPA, TNT and tetryl were 23.14, 47.07 and 52.30, respectively. Continuous extraction of DPA was done with the help of flash chromatography combined with MIP and showed more than 98% recovery. MIP has a good regeneration performance and could maintain almost the same adsorption capacity even after three adsorption– desorption cycles.



**Fig. 20: Schematic for the development of DPA–MIP and its combination with flash chromatography.**

In another study, the synthesis of a Pb(II) ion-imprinted interpenetrating polymer network (II-IPN) by simultaneous polymerization for selective extraction of Pb(II) from printed-circuit-board (PCB) recycling unit wastewater is reported (Fig. 21). Initially, a polymer network was synthesized by polymerization of methacrylic acid (monomer) and ethylene glycol dimethacrylate (cross-linker) and a second polymer network by chitosan (complexing monomer) and tetraethyl orthosilicate (cross-linker). The chemical structure and morphology of the II-IPN were analyzed using Fourier transform infrared, field-emission scanning electron microscopy, atomic force microscopy, and transmission electron microscopy. The interaction of the functionality in the II-IPN with Pb(II) through chelation was studied by X-ray photoelectron spectroscopy analysis. The maximum adsorption capacities for II-IPN and nonimprinted interpenetrating polymer network were  $37.5$  and  $10.3 \text{ mg g}^{-1}$ , respectively. The largest selectivity coefficient for Pb(II) in the presence of W(VI) was 161.58. The developed

Pb(II) II-IPN was successfully employed for selective extraction of Pb(II) from PCB recycling unit wastewater.



**Fig. 21:** Schematic for the removal of Pb from developed IIP.

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- P.E. Hande, Development of Molecularly Imprinted Polymers for Sensing and Removal of Toxic Solutes, PhD Thesis 2017.

## 2) Wastewater treatment by ion exchangers/adsorbents

[Place: Defence Institute of Advanced Technology (DU), Ministry of Defence, Pune, India]

In the past decades, human needs were responsible for the generation of various technologies, and industries have adopted and applied them to create products. Meanwhile, such industrial and civil activities have also led to produce enormous wastes, and their improper disposal resulted as air, water, and soil pollutions. Amongst the wastes, contaminations of heavy metal ions in water bodies due to either leather tanning, metal finishing, etching and/or electroplating processes have imposed serious health threats on the flora and fauna. Especially, metal ions and metal oxyanions along with their counter parts (e.g. nitrates) are the most common contaminants in wastewater. Moreover, many of these heavy metal ions are rare ones (e.g. W(VI)), and therefore, their selective recovery from secondary sources would be beneficial in conserving limited resources.

Adsorption or ion-exchange is a fundamental and economically viable process for the treatment of wastewater because of its several advantages such as high removal efficiency, low energy demand, less chemical investment, and reusability. In order to recover metal ions via adsorption, several studies were carried out for the development of adsorbents such as activated carbon, clays, nanomagnetic particles, and low-cost biosorbents. However, these adsorbents suffer from low adsorption capacity and selectivity because of having less porosity, low surface area, and lack of functional groups. Meanwhile, silica-based materials have been provided as sustainable materials in treating wastewater due to their high surface areas, hydrothermal stabilities, and the availability of required functional groups.

The understanding of structural conformation and adsorption capacities of silica-based materials has provided the prospects and ideas to develop better adsorbents via polymer, ionic liquid and biomolecule immobilizations on various silicas. In that case, we have initially carried out synthesis of low-cost adsorbents (composites) via the combination of amine-formaldehyde resins and the abundant silica gels by means of coating. Indeed, immobilized amine groups on the silica surface, once gets protonated at certain pH, have provided adsorption sites for the metal oxyanions [Cr(VI) and W(VI)] via electrostatic interaction and/or ion-exchange (Fig. 22).

In order to enhance the adsorption capacity and selectivity, further developed IL-functionalized mesoporous organosilicas (IL-PMOs) with *in-situ* PEG-linked bis-imidazolium chloride bridged framework. In this case, the role of silicate was studied as a cross-linker which can affect the loadings of IL-precursor, and its impact on the textural conformation of PMOs (Fig. 23). These adsorbents with high surface area and functionality have shown high removal capacities for the separation of W(VI) from aqueous stream. With the concept of

designing a dicationic framework of silica adsorbents, we have prepared L-proline functionalized dicationic frameworked mesoporous organosilica (Fig. 23). This bifunctional material was deliberately introduced for the treatment of aqueous stream containing both toxic cations ( $\text{Pb}^{2+}$ ) and anions ( $\text{NO}_3^-$ ).

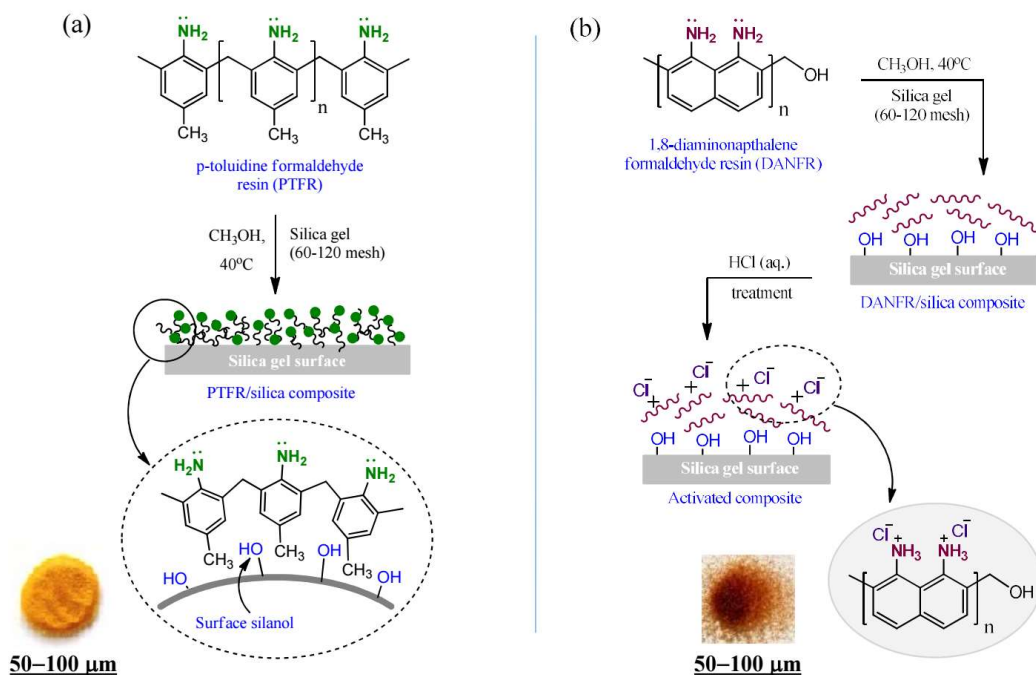


Fig. 22: Development of silica-based adsorbents (PTFR and DANFR).

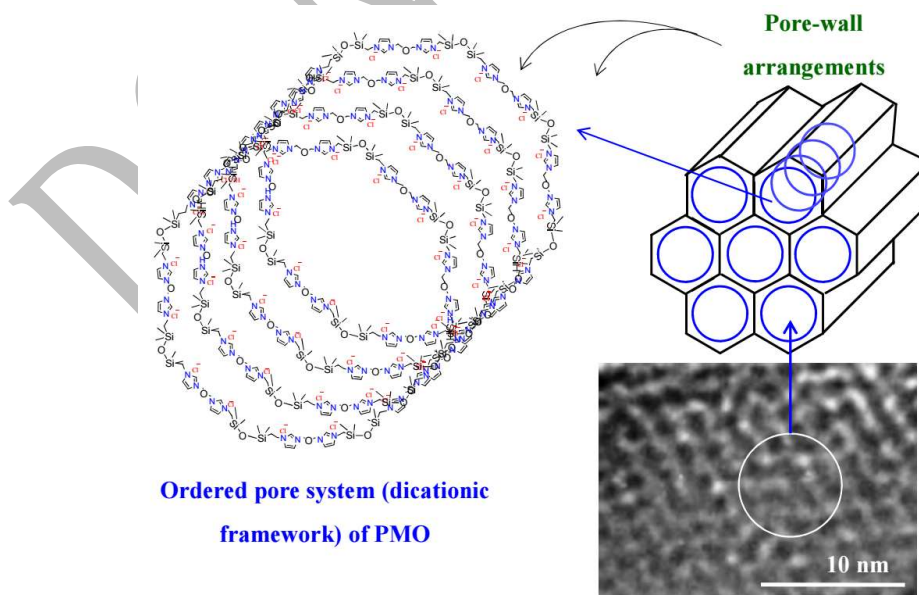


Fig. 23: Developments of periodic mesoporous organosilicas (PMOs).

Notably, in most of the cases, the aforementioned materials were successfully regenerated and reused many a times, which fulfils the objective of designing highly compatible and sustainable silica-based adsorbents for the removal of heavy metal ions.

**Sponsored Projects/ Patents/ Publications/ Thesis:**

- a) S.K. Das, M.K. Dinker, P.S. Kulkarni, PEG-linked bis-imidazolium and polyhedral oligomeric based silsesquioxanes as ion exchangers, *Microporous and Mesoporous Materials* 343 (2022) 112185.
- b) M.K. Dinker, T.G. Ajithkumar, P.S. Kulkarni, L-Proline Functionalized Dicationic Framework of Bifunctional Mesoporous Organosilica for the Simultaneous Removal of Lead and Nitrate Ions, *ACS Sustainable Chemistry & Engineering*, 5(5) (2017) 4188.
- c) M.K. Dinker, P.S. Kulkarni, Insight into the PEG-linked bis-imidazolium bridged framework of mesoporous organosilicas as ion exchangers, *Microporous and Mesoporous Materials*, 230 (2016) 145.
- d) M.K. Dinker, P.S. Kulkarni, "Temperature based adsorption studies of Cr(VI) using p-toluidine formaldehyde resin coated silica", *New Journal of Chemistry*, 39 (2015) 3687.
- e) M.K. Dinker, P.S. Kulkarni, "Recent Advances in Silica-Based Materials for the Removal of Hexavalent Chromium: A Review", *Journal of Chemical & Engineering Data*, 60(9) (2015) 2521.
- f) M.K. Dinker, N.V. Patil, P.S. Kulkarni, A diamino based resin modified silica composite for the selective recovery of tungsten from wastewater, *Polymer International*, 65 (2016) 1387.

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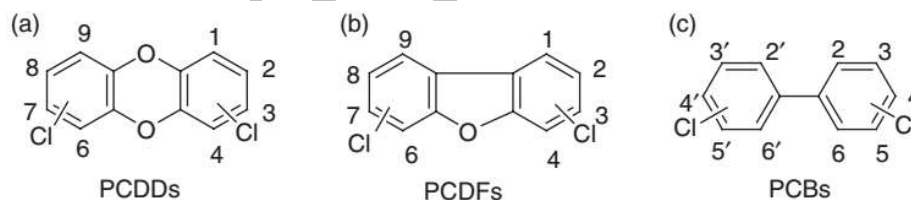


### 3) Treatment of dioxins

[Place: Institute of Superior Technology (IST), Lisbon, Portugal and Centre for Green Chemical Processes, New University of Lisbon, Portugal]

Dioxins are a class of structurally and chemically related polyhalogenated aromatic hydrocarbons that mainly include polychlorinated dibenzo-p-dioxins (PCDDs or dioxins), dibenzofurans (PCDFs or furans), and the 'dioxin-like' biphenyls (PCBs). They are nonpolar, water insoluble, lipophilic, and stable chemicals. Dioxins are unintentional by-products of several chemical processes and usually occur as a mixture of congeners. Their presence in the incinerator fly ash samples was first reported in the year 1977 and had come to public attention in the year 1976 when an explosion at ICMESA factory in Seveso, Italy, deposited these chemicals over an area of 2.8 km<sup>2</sup>.

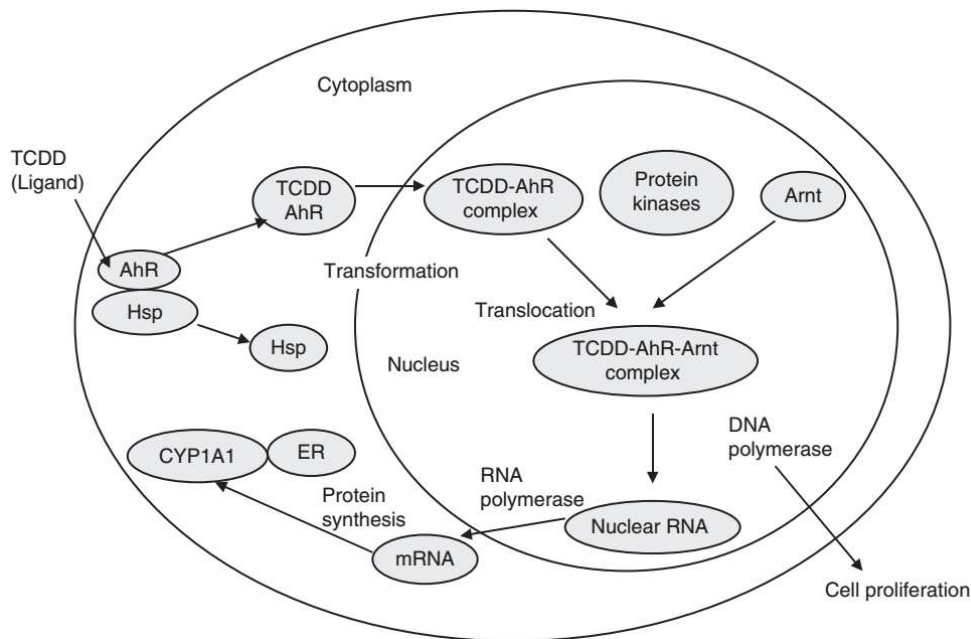
The chlorinated dibenzo-p-dioxins and dibenzofurans are tricyclic aromatic compounds that are quite similar structurally. There are 75 possible different positional congeners of PCDDs, 135 different PCDF congeners and 209 possible PCB congeners. Physical and chemical properties of each congener vary according to the degree and position of chlorine substitution. Figure 24 depict the basic structural formula of PCDDs, PCDFs, and PCBs together with the numbering convention at the positions on benzene rings where chlorine or other halogen atoms can be substituted. The isomer 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD) has been called the most toxic synthetic compound known to human being.



**Fig. 24: Chemical structures of (a) PCDDs, (b) PCDFs, and (c) PCBs.**

**Toxicity of Dioxins:** The general population exposure to dioxins chemicals occurs as exposure to a mixture of different congeners. However, the effects are mediated through an interaction of dioxins with the aryl hydrocarbon (Ah) receptor presenting inside the cell. The Ah receptor is prone to binding with halogenated aromatic hydrocarbons, including dioxins and PCBs that can cause changes in gene expression, affecting cell growth, form, and function. Figure 25 depicts a simple schematic model of action of dioxin inside cell. The dioxins can induce a broad spectrum of biological responses, including induction of gene expression for cytochrome P450, for example, CYP1A1, and CYP1A2, disruption of normal hormone signaling pathways, reproductive and developmental defects, wasting syndrome and immune suppression, liver damage, and cancer. These depend on species, strain, age, and gender. Briefly, it indicates that the inappropriate modulation of gene expression

represents the initial steps in a series of biochemical, cellular, and tissue changes that result in the toxicity observed.



**Fig. 25: A schematic model of the action of dioxins in cell.**

It is observed that the dioxins and dioxin-like chemicals are predominantly produced by thermal processes such as incineration and combustion at concentrations in the range of 10 to 100 ng of I-TEQ/kg (I-TEQ = international toxic equivalents). A new approach for the removal of dioxins from high-temperature vapor streams using facilitated supported ionic liquid membranes (SILMs) is proposed (Fig. 26). The use of ceramic membranes containing specific ionic liquids, with extremely low volatility, for dioxin removal from incineration sources is proposed owing to their stability at very high temperatures. Supported liquid membranes were prepared by successfully immobilizing the ionic liquids ([Aliquat][DCA]) and ([Omim][DCA]) inside the porous structure of ceramic membranes. The porous inorganic membranes tested were made of titanium oxide ( $\text{TiO}_2$ ), with a nominal pore size of 30 nm, and aluminum oxide ( $\text{Al}_2\text{O}_3$ ), with a nominal pore size of 100 nm. The ionic liquids were characterized, and the membrane performance was assessed for the removal of dioxins. Different materials (membrane pore size, type of ionic liquid, and dioxin) and different operating conditions (temperature and flow rate) were tested to evaluate the efficiency of SILMs for dioxin removal. All membranes prepared were stable at temperatures up to 200 °C. Experiments with model incineration gas were also carried out, and the results obtained validate the potential of using ceramic membranes with immobilized ionic liquids for the removal of dioxins from high temperature vapor sources.

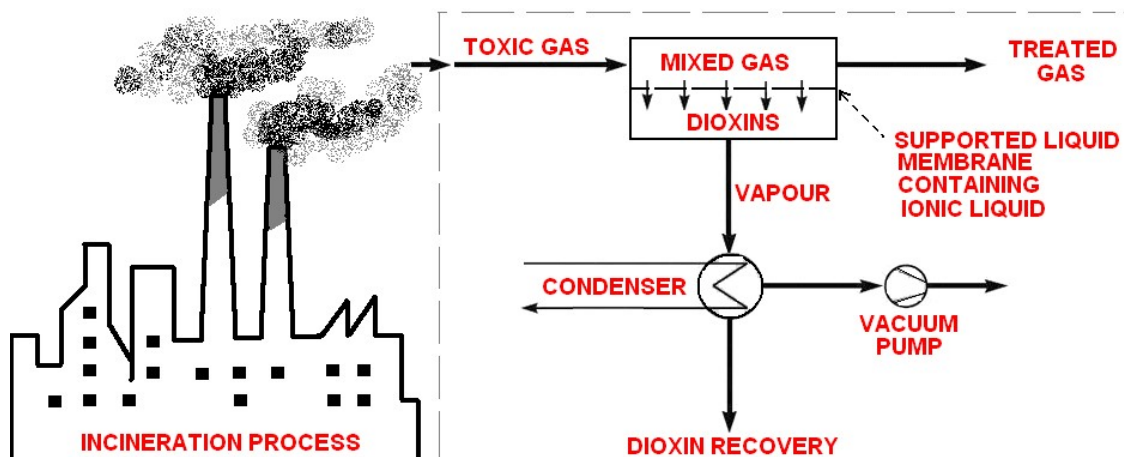


Fig. 26: A proposed method for the treatment of dioxins.

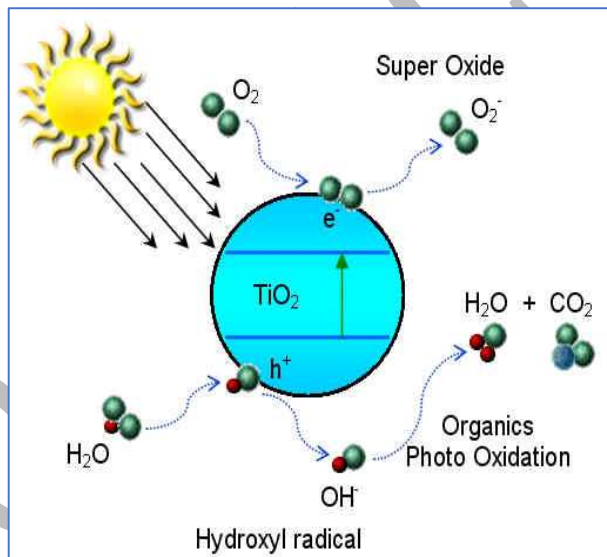
**Sponsored Projects/ Patents/ Publications/ Thesis:**

- a) Prashant S. Kulkarni, Luís C. Branco, João G. Crespo & Carlos A. M. Afonso (2007). Removal of dioxins and their analogs from gas flows comprises trapping via synthetic membranes and high stability ionic liquids. Patent Granted (No. PT103717).
- b) P.S. Kulkarni, et al. "Supported liquid membranes for the removal of dioxins", *Environmental Science & Technology*, 46(1) (2012) 462.
- c) P.S. Kulkarni, et al. "Capture of Dioxins by Ionic Liquids", *Environmental Science & Technology*, 42 (2008) 2570.
- d) P.S. Kulkarni, et al. "Dioxins Sources & Current Remediation Technologies – A Review", *Environment International*, 34 (2008) 139.
- e) Kulkarni PS (2019) Dioxins. In: Nriagu JO (ed.) *Encyclopedia of Environmental Health - 2<sup>nd</sup> Edition.*, Burlington (USA): ELSEVIER.
- f) Kulkarni PS (2015) Dioxins (Chapter 20). In: Lackner M., Winter F. and Agarwal A. (ed.) *Handbook of Combustion volume. 2: Combustion Diagnostics and Pollutants*, ISBN: 978-3-527-32449-1, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim (Germany).
- g) Kulkarni PS, Crespo JG and Afonso CAM (2011) Dioxins. In: Nriagu JO (ed.) *Encyclopedia of Environmental Health*, volume 2, pp. 83–92, ISBN: 978-0-444-52272-6, Burlington (USA): ELSEVIER.

#### 4) Photocatalytic degradation of organics

[Place: Defence Institute of Advanced Technology (DU), Pune, India and National Chemical Laboratory, Pune, India]

Photocatalysis is a green and promising redox process for mitigating organic pollutants in contaminated water since it completely mineralizes the pollutant into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  without forming any hazardous byproducts (Fig. 27). The semiconducting materials such as  $\text{TiO}_2$ ,  $\text{ZnO}$ , and  $\text{WO}_3$  are extensively used as photocatalysts. They accelerate the light-induced photochemical reactions and have a unique electronic structure of band gap energy ( $E_g$ ). The  $E_g$  is the difference between the filled valence band and an empty conduction band. In photocatalysis, electron-hole pairs are generated when incident light photon energy is greater than or equal to  $E_g$ . Nevertheless, most of the semiconductors have a large  $E_g$  (approx. 3.5–2.7 eV). Out of the total solar spectrum UV range, only 4% is utilized, whereas of the visible range, nearly 40% remains unutilized for solar energy applications. Further, in photocatalysis, a few concerns are associated with the faster electron-hole recombination rate, ineffective charge carrier separation, and photocorrosion.



**Fig. 27: Photocatalytic degradation mechanism.**

In a typical investigation, a magnetically separable, barium hexaferrite ( $\text{BaFe}_{12}\text{O}_{19}$ ) nanoplatelets were synthesized at various temperatures by cost-effective, molten salt technique and its photocatalytic activity was compared with commercially available  $\text{TiO}_2$ .  $\text{BaFe}_{12}\text{O}_{19}$  nanostructures were characterized by using UV-vis-DRS, FESEM, XRD, BET, and Raman and further, subjected to photocatalytic degradation of an organic pollutant, hexahydro-1,3,5-trinitro-1,3,5 triazine (RDX) under UV and visible light. The reaction parameters, degradation kinetics, and mechanism were thoroughly studied, and optimum

reaction conditions were evaluated. The degradation products were analyzed by HPLC, LCMS, and TOC. The  $\text{BaFe}_{12}\text{O}_{19}$ -800 °C nanoplatelets ( $0.6 \text{ g}\cdot\text{L}^{-1}$ ) with UV-vis lamp irradiation were efficient and economical to degrade  $40 \text{ mg}\cdot\text{L}^{-1}$  of RDX below the discharge limits ( $<0.035 \text{ mg}\cdot\text{L}^{-1}$ ) in 300 min whereas  $\text{TiO}_2$  showed  $4 \text{ mg}\cdot\text{L}^{-1}$  of unreacted RDX at similar conditions. Kinetic rate of  $\text{BaFe}_{12}\text{O}_{19}$  and  $\text{TiO}_2$  were observed to be  $0.017$  and  $0.003 \text{ min}^{-1}$ , respectively. Magnetic separation of  $\text{BaFe}_{12}\text{O}_{19}$  for recovery and recycling is also reported (Fig. 28).

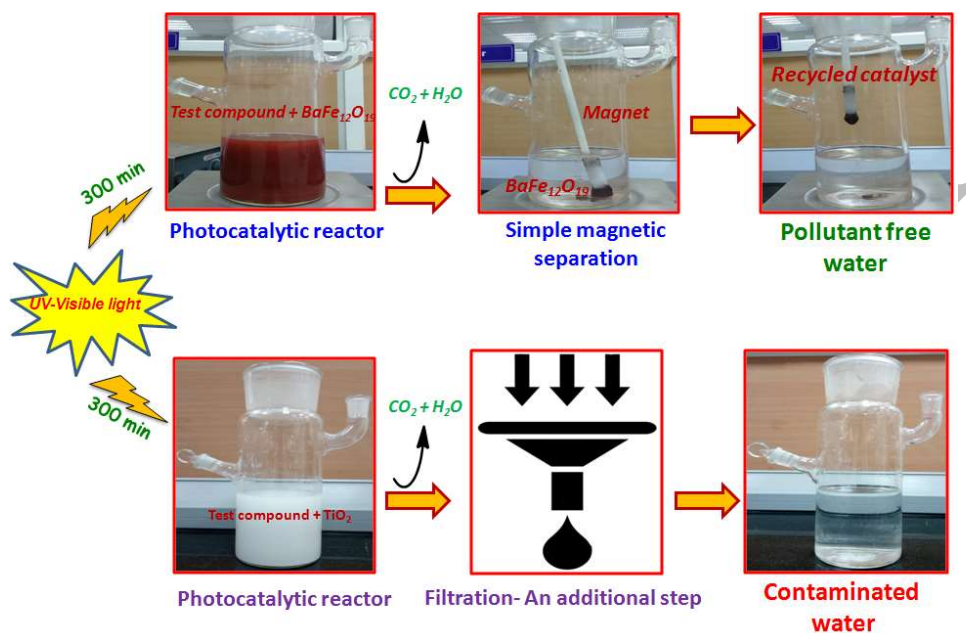


Fig. 28: Schematic for the treatment of contaminated wastewater using photocatalysis.

#### Sponsored Projects/ Patents/ Publications/ Thesis:

- S.S. Raut, Santhosh Kumar A., A. Jambhale, A.C. Abhyankar, P.S. Kulkarni, Enhanced photocatalytic activity of magnetically separable barium hexaferrite nano-platelets, *Industrial and Engineering Chemistry Research*, 57 (48) (2018) 16192.
- S.S. Raut, S.P. Kamble, P.S. Kulkarni, Improved photocatalytic efficiency of  $\text{TiO}_2$  by doping with tungsten and synthesizing in ionic liquid: precise kinetics-mechanism and effect of oxidizing agents, *Environmental Science and Pollution Research* 28(14) (2021) 17532.
- S.S. Raut, P.S. Kulkarni, Photodegradation of an ammonium ionic liquid: spiking in urban wastewater and comparison with aromatic ionic liquids, *Environmental Science: Water Research & Technology* 7 (2021) 1723.
- K. Yadav, S. S. Raut, T. U. Patro, A. C. Abhyankar, P. S. Kulkarni, Annealing Temperature- and Morphology-Controlled Development of Nickel Cobaltite Nanoneedles for Photocatalytic Degradation of Nitroaromatics, *Industrial & Engineering Chemistry Research*, 61 (2022) 4273.
- S.S. Raut, Synthesis of nanomaterials for the dechlorination and Photocatalytic degradation of organic pollutants, PhD Thesis (2020).

## 5) Desulphurization of Petroleum Fuels

[Place: <sup>1</sup>Centre for Green Chemical Processes, New University of Lisbon, Portugal; <sup>2</sup>Defence Institute of Advanced Technology (DU), Ministry of Defence, Pune, India]

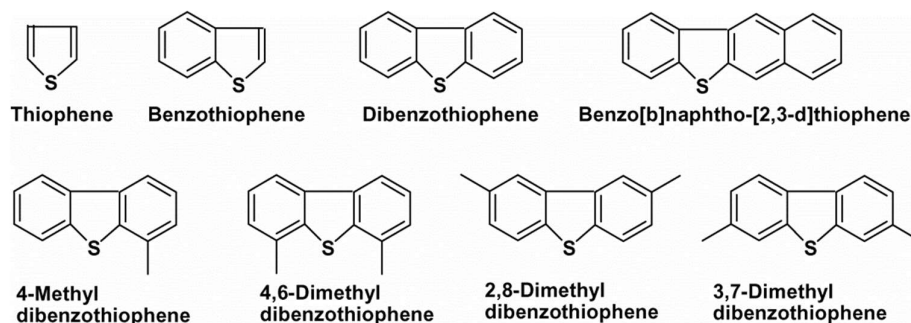
Production of ultra-low-sulfur diesel (ULSD) has become a major task of refineries all over the world. The presence of sulfur compounds in diesel fuel has shown an adverse impact on the environment and hence, it is getting ample attention from the media and scientific community. It is because sulfur-bearing compounds are converted to SO<sub>x</sub> during the combustion of car engines. This conversion not only results in acid rain, but also high contents of sulfuric oxides in exhaust fumes lowers the efficiency of catalytic converters in cars. Sulfuric oxides also poison catalysts in catalytic converters used for reducing CO and NO<sub>x</sub> emissions and this severely affects environment.

Therefore, governments all over the world are implementing stringent standards for the production of ULSD from petrochemical industries. The EU legislation set the upper limit of sulfur content in diesel fuel to 10 ppm and in 2006 the US Environmental Protection Agency (EPA) reduced the limit for sulfur content of diesel fuel to 15 ppm. It is also important to note that deep desulfurization is not only used for producing clean fuels to meet the new legislation standards, but also for producing sulfur-free hydrogen used in fuel-cell devices, in which the hydrogen can be produced potentially through reforming fuel oils. Fuel cell devices should run with zero sulfur content because sulfur can irreversibly poison the precious metal catalysts and electrodes used.

The hydrodesulfurization (HDS) process has been used for the past several years to eliminate sulfur compounds for industrial purposes (Fig. 29). The HDS process uses Co–Mo/Al<sub>2</sub>O<sub>3</sub>, Ni–Mo/Al<sub>2</sub>O<sub>3</sub> or Ni–W/Al<sub>2</sub>O<sub>3</sub> catalysts for the conversion of organic sulfur to H<sub>2</sub>S. The shortcomings of this method are: (i) it is operated at very high temperatures (300–400 °C) and pressures (20–100 atm of H<sub>2</sub>), (ii) octane/cetane number is reduced due to hydrogenation side reactions, and (iii) it is efficient for the removal of thiols, sulfides and thiophenes, but less effective for removing refractory sulfur compounds such as benzothiophene, dibenzothiophene, and their alkyl derivatives. Fig. 30 shows structures of the refractory sulfur compounds that are present in the petroleum streams. Total removal of such compounds is vital to meet the current stringent regulations. Their lower reactivity to the HDS process is mainly attributed to the steric hindrance. For these reasons, alternate desulfurization processes are absolutely necessary for producing clean fuels.



**Fig. 29: Hydrodesulfurization (HDS) process used for removal of sulfur compounds**



**Fig. 30: Refractory sulfur compounds present in untreated fuel.**

Therefore, the removal of the refractory sulphur compound with the help of non-conventional sulfur removal techniques like EDS (extractive desulphurization) and ODS (oxidative desulphurization) were studied. The work was aimed at developing a method to completely strip off sulfur containing compounds from diesel fuel. An increase in the alkyl side-chain for imidazolium-based ILs improves sulfur removal efficiency; therefore, an IL with a long alkyl chain was selected. A hydrophobic, low-viscosity, room temperature ionic liquid, [OMIM][NTf<sub>2</sub>] was employed as an extractant with hydrogen peroxide and acetic acid as oxidant and catalyst, respectively. Among the studied desulfurization schemes, the two-step ODS was found to be most effective in terms of D.E, oil, and IL recovery for desulfurization of model oil. Complete desulfurization of model oil was achieved by two step ODS within 6 hours by utilization of a low quantity of the ionic liquid. The optimized scheme was further employed in desulfurization of mixed gas oil which also showed potential of the method in desulphurization of diesel fuels.

**Sponsored Projects/ Patents/ Publications/ Thesis:**

- a) P.S. Kulkarni and C.A.M. Afonso, "Deep desulfurization of diesel fuel using ionic liquids: current status and future challenges – Critical Review", *Green Chemistry*, 12 (2010) 1139.
- b) Mr. Tushar Thakur, Oxidative desulphurization of Diesel Fuel Using Ionic Liquid, MTech Thesis (2020).

## 6) Hydrodechlorination of organic contaminants

[Place: Defence Institute of Advanced Technology (DU), Ministry of Defence, Pune, India and National Chemical Laboratory, Pune, India]

In several countries, chloro-aromatic compounds are widely used in dyes, agriculture, and pharmaceutical industries. The manufacturing of different chlorinated compounds substantially generates a large amount of chlorinated organic waste. The waste generated by these industries is a significant threat to aquatic and human life as this type of compound tends to persist in the environment over a long period of time. Due to the low biodegradability of chloro-aromatic compounds, they are considered a major pollution source in an ecosystem. Prolonged exposure to chloro-aromatic compounds causes genetic disorders, throat-related diseases, birth defects, endocrine dysfunction, infertile immune suppression, reproductive dysfunction, and cancer.

Catalytic hydrodechlorination (HDC) can be the best economical process for the treatment of chloro-aromatic compounds. The HDC only removes Cl from the structure of the pollutant and results in less hazardous products compared to the parent compounds. The HDC is a clean and low-cost process that operates in mild conditions (Fig. 31). The chief advantage is that the HDC process can be stopped at a desired reaction intermediate without the formation of by-products. Modern chemical research always prefers to recover the product from waste that will add value to the industry than destroy it. Researchers have been working on the HDC for the past several years. The use of zero-valent iron (ZVI) for the HDC of chlorinated compounds (CPs) has been reported; however, the limitation of ZVI is that it leads to the oxide layer formation on the catalyst's surface. The appearance of an oxide layer reduces the activity of the catalyst. Furthermore, the use of noble metals such as Pd, Pt, and Rh for the HDC process is well known due to their several advantages, including high reactivity and long-life span. However, the process with noble metal as a catalyst is a high-priced way of wastewater treatment that has no further extension in actual wastewater treatment.

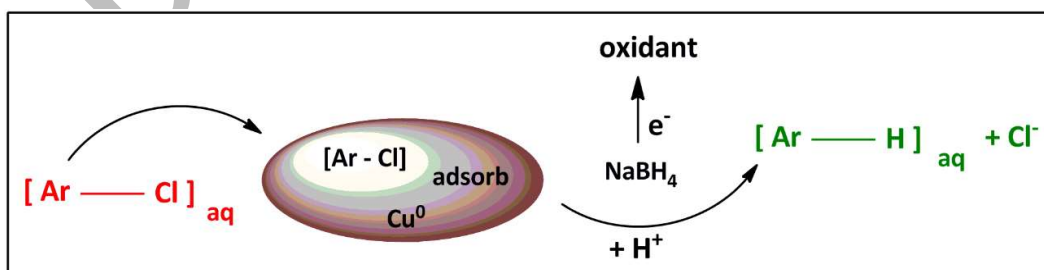


Fig. 31: Mechanism of catalytic hydrodechlorination of chloroaromatic compounds.



The 4-chloro-2-amino phenol (4C2AP) bearing wastewater is produced while manufacturing dyes and pharmaceutical ingredients. Ni- and Cu-based cost-effective catalysts were developed, typically characterized, and subjected to hydrodechlorination (HDC) of 4C2AP. The role of reducing agents, concentration, pH of wastewater, presence of salt, reaction temperature, catalyst reuse, and the kinetics was investigated. A selective makeover of 2-amino phenol (2AP) was analyzed by HPLC, LCMS, and NMR. A complete HDC of 4C2AP with remarkable selectivity (98%) toward 2AP was achieved using a Ni<sup>0</sup> catalyst and NaBH<sub>4</sub> at room temperature (Fig. 32). It is observed that the alkaline condition, the presence of salt, and a high reaction temperature favor the HDC process. A maximum of 1 g L<sup>-1</sup> of the Ni<sup>0</sup> loading is found to be sufficient to dechlorinate the pollutant. It can be concluded that the catalytic HDC is a technically viable and inexpensive process for the conversion of 4C2AP into a valuable product, 2AP.

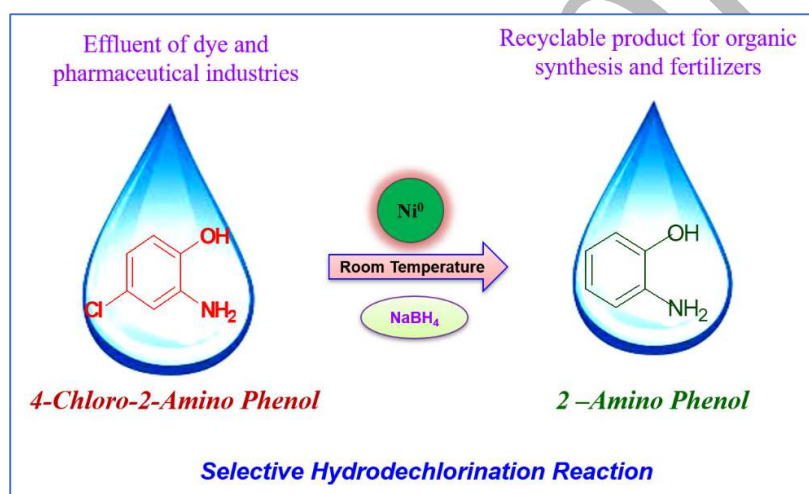


Fig. 32: Selective hydrodechlorination of 4-chloro 2-amino phenol.

#### Sponsored Projects/ Patents/ Publications/ Thesis:

- S.S. Raut, S.P. Kamble, P.S. Kulkarni, Efficacy of zero-valent copper (Cu<sup>0</sup>) nanoparticles and reducing agents for dechlorination of mono chloroaromatics, *Chemosphere*, 159 (2016) 359.
- S.S. Raut, R. Shetty, N.M. Raju, S.P. Kamble, P.S. Kulkarni, Screening of zero valent mono/bimetallic catalysts and recommendation of Raney Ni (without reducing agent) for dechlorination of 4-chlorophenol, *Chemosphere*, 250 (2020) 126298.
- R.R. Shetty, R.S. Raut, P.S. Kulkarni, S.P. Kamble, Hydrodechlorination of 4-Chloro-2-Aminophenol into a Recyclable Product Using Ni- and Cu-Based Catalysts, *Industrial and Engineering Chemistry Research* 61 (39) (2022) 14433.

## 7) Separation of Carbon dioxide (CO<sub>2</sub>)

[Place: <sup>1</sup>Centre for Green Chemical Processes, New University of Lisbon, Lisbon, Portugal;  
<sup>2</sup>Defence Institute of Advanced Technology (DU), Ministry of Defence, Pune, India]

Global warming is one of the most challenging issues in front of the scientific community of all over the world. The rise in the level of atmospheric carbon dioxide (CO<sub>2</sub>) is the significant cause of the is imminent risk and therefore, mitigating the CO<sub>2</sub> concentration is the major aspect of this challenge. A simple and proficient way to decrease the CO<sub>2</sub> concentration is to capture the same prior to release in environment. Although various methods are existing, solvent absorption is by far the most widely utilized technique to capture and reduce CO<sub>2</sub> emissions. The solvent, alkanolamine is currently used by the industry however, it has several limitations such as corrosive nature, toxicity, degradability and high energy requirements for regeneration. In an attempt to find alternative solvents with advantageous properties, polymeric ionic liquids (PILs) have been proposed as a new media for CO<sub>2</sub> capture.

In this regard, the synthesis and characterization of new series of PIL with tetraalkylammonium centre and varying anion centre have been incorporated in this study. Poly(ethylene glycol) (PEG) was modified to prepare amine substituted PEG diacrylate which was quaternized with 1-bromopentane to yield the PIL, PD-Br. The PIL products such as PDNTf<sub>2</sub> and PDBF<sub>4</sub> were obtained by metathesis of PDBr with respective salt. The developed products were thoroughly analyzed by using FTIR, <sup>1</sup>H and <sup>13</sup>C NMR, elemental analysis, density meter and viscosity meter. The thermal properties of PILs were investigated by using DSC and TGA. The thermal degradation behaviour of the PILs shows two-stage decomposition with thermal stability till 150 °C. Further, the CO<sub>2</sub> sorption of the PILs was studied by the pressure drop method. The sorption study indicates increased absorption of CO<sub>2</sub> with increasing pressure. The equilibrium is attained within 40 min thereby

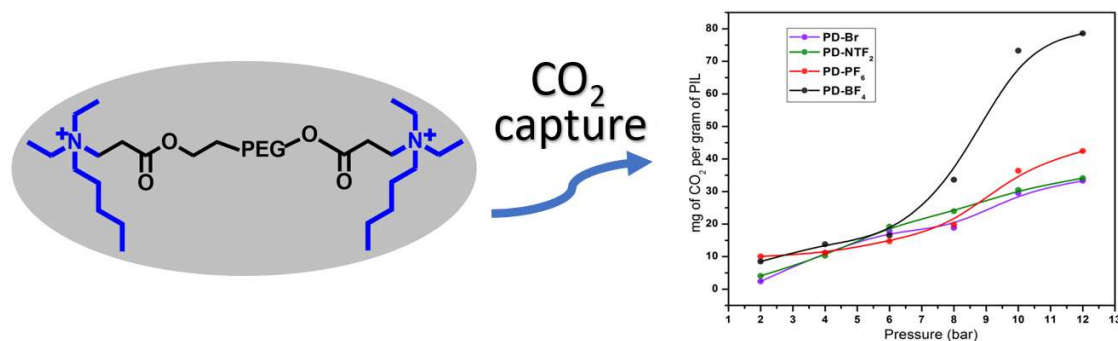
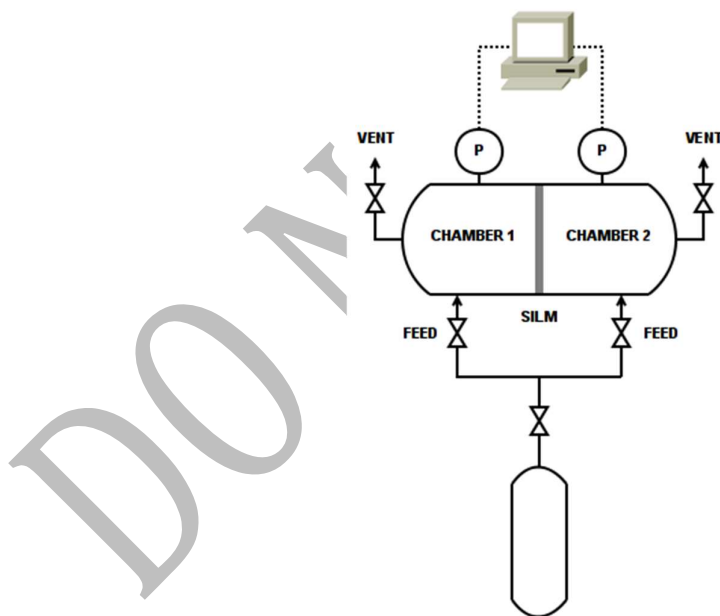


Fig. 33: Schematics of CO<sub>2</sub> Capture by using tetraalkylammonium based dicationic ionic liquid.

showing fast absorption rate (Fig. 33). The highest sorption capacity has been exhibited by PIL with  $\text{BF}_4$  anion. The regeneration of PIL was also investigated by using FTIR. This study indicates the versatile nature of tetraalkylammonium based dicationic PIL making it a potential material for multiple applications including  $\text{CO}_2$  capture.

In order to study the facilitated transport of  $\text{CO}_2$  (inside supported ionic liquid membrane), the permeability experiments were carried out in the experimental apparatus shown in Figure 34. It is composed by a stainless-steel cell with two identical chambers separated by the supported ionic liquid membrane. The permeability was evaluated by pressurizing one of the chambers (up to 0.5 bar) with a single gas followed by the measurement of the pressure change in both chambers over time, using two pressure transducers. These measurements were made at constant temperature,  $30^\circ\text{C}$ , using a thermostatic bath. In these experiments the gases tested were air and  $\text{CO}_2$ . The membrane weight was measured, before and after the gas permeation experiments, in order to evaluate the stability of these membranes. It was observed that the permeability of air is one order of magnitude lower than  $\text{CO}_2$  permeability. Considering the permeability and selectivity results, the hydrophilic membrane immobilized with the ionic liquid [BIM][ace] showed the highest permeability.



**Fig. 34: Scheme of gas separation apparatus to measure the permeability in SILMs.**

**Sponsored Projects/ Patents/ Publications/ Thesis:**

- a) Supported Ionic Liquid Membranes Designed for the Removal or Capture of Dioxins,  $\text{CO}_2$  &  $\text{SO}_2$ . 2<sup>nd</sup> Int. Conference on Green Process Engineering
- b) PS Kulkarni et al. Tetraalkylammonium-based dicationic ionic liquids (ILs) for  $\text{CO}_2$  capture, *New Journal of Chemistry* 47 (2023) 12944.

## 8) Toxicological study of new solvents and molecules

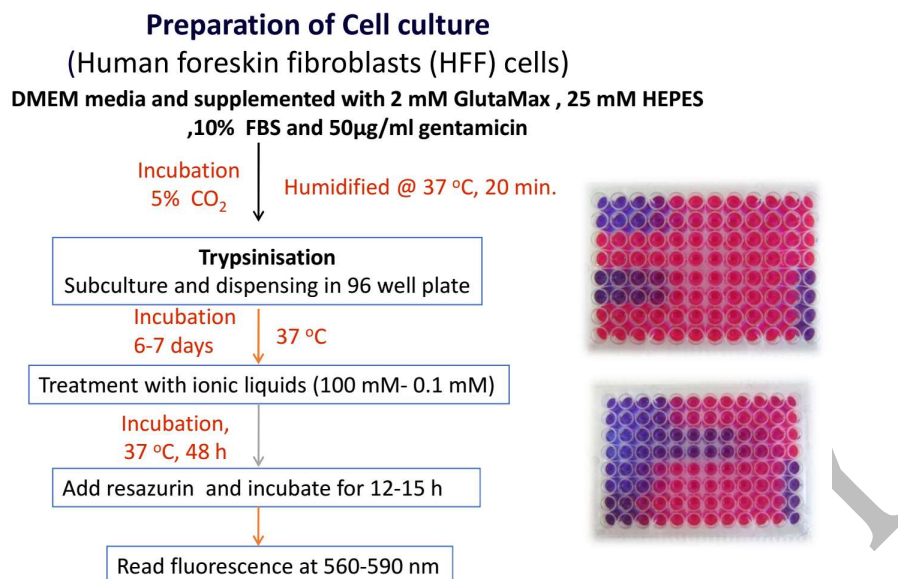
[Place: <sup>1</sup>Defence Institute of Advanced Technology (DU), Ministry of Defence, Pune, India; <sup>2</sup>Centre for Green Chemical Processes, New University of Lisbon, Lisbon, Portugal]

Toxicology is the study of the adverse effects of chemical substances on living organisms. The relationship between dose and its effects on the exposed organism is of high significance in toxicology. Various new ionic liquids (ILs) were developed in the laboratory and therefore it was thought to investigate the toxicity behavior of these ionic liquids (Fig. 35). The cytotoxicity of hypergolic ILs is very essential to be addressed to the society in order to avoid any jeopardy to the professional person involved in handling such ILs during synthesis, transportation and application in propulsion field. The cytotoxicity of twenty hypergolic ILs (containing imidazolium and pyridinium core) were investigated for the first time on human foreskin fibroblast (HFF cell) line under specific conditions and were studied at various concentrations (0.1 to 100 mM). The effect of various concentration of ILs on HFF cell and inhibited concentration for 50% cell ( $IC_{50}$ ) were studied in detail.



Fig. 35: Cationic structures of the investigated ionic liquids.

A colorimetric reagent resazurin (oxidation-reduction indicator) was used for cytotoxic assay. The assay accounts for number of viable cells that possess metabolic capacity to convert the non-fluorescent redox indicator, resazurin into its highly fluorescent product resofurin. The cells were trypsinized, counted and then plated out in 96 well plates (NUNC) ( $\sim 5 \times 10^3$ - $8 \times 10^3$  cells/ well). These plates were allowed to incubate for 6-7 days to attain confluent cell growth. Then, the cells were treated with serially diluted concentrations of all the ILs from 100 mM to 100  $\mu$ M in DMEM without FBS in duplicates along with 20% DMSO. The untreated cells considered as positive and negative controls. The cells with serial dilution of ILs were incubated for 48 h and then, resazurin (10 mM stock in  $H_2O$ ) was added to each well, making its final concentration 100  $\mu$ M. After 12-15 h, production of resofurin was detected via fluorescence using Thermo varioskkan plate reader at excitation of 560 nm and emission at 590 nm (Fig. 36).



**Fig. 36: Cytotoxicity experimental investigation.**

This was the first initiative to study or assess the cytotoxicity of hypergolic ILs on HFF cells, especially the never ever probed BH<sub>3</sub>CN based ILs. The investigations revealed that ILs with concentration more than 12.5 mM resulted in 100% proliferation of cell line. For the same anion, pyridinium in comparison to imidazolium cationic core was found to be more toxic. In very much agreement with literature data, it was observed that length of the alkyl substituent on the cation had pronounced effect on the toxicity. Hypergolic BH<sub>3</sub>CN anion based ILs were evaluated to be least toxic in comparison with DCA anion based ILs. In comparison with known [BF<sub>4</sub>], [NTf<sub>2</sub>], [Br], [DCA] anion based conventional ILs, [BH<sub>3</sub>CN] based ILs were found to be less toxic which can be a major breakthrough in the field of hypergolic IL fuels that could be used for space propulsion, in future. Therefore, the cytotoxicity of these hypergolic ILs is equivalent to some of the routinely used organic solvents in chemical laboratory. It is necessary to undertake simple chemical safety precautions during the handling of hypergolic ILs.

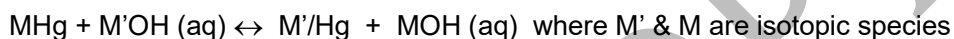
**Sponsored Projects/ Patents/ Publications/ Thesis:**

- a) Vikas Bhosale, Studies on ionic liquid based hypergolic fuels, PhD Thesis 2018.
- b) R.F.M. Frade, A.A. Rosatella, C.S. Marques, L.C. Branco, P.S. Kulkarni, N.M.M. Mateus, C.A. Afonso, C.M.M. Duarte "Toxicological evaluation on human colon carcinoma cell line (CaCo-2) of ionic liquids based on imidazolium, guanidinium, ammonium, phosphonium, pyridinium & pyrrolidinium cations" *Green Chemistry*, 11 (2009) 1660.

## 9) Detection of air-borne mercury

[Place: Bhabha Atomic Research centre - DAE, Mumbai, India]

Mercury is highly toxic metal ion due to its large vapor pressure. The present mercury surveillance-work, stems from the large-scale use of mercury in the division, which poses an exposure risk to the personnel and hazard to environment. Mercury being a hazardous liquid metal has very high vapor toxicity. Such a large-scale use of mercury is inexorable for a certain-isotopes-separation-process developed in this division. It is based on the principle of chemical-exchange and inevitable requires the of two immiscible phases (viz. M/Hg and MOH aq.) contacting each other a suitably packed column in a counter-current fashion. The essential chemical-exchange-reaction involved can be represented as under:



For the separation-factor “K” to be substantially different from unity, it is a theoretical prerequisite that not only must the free energies of the isotopic species involved be different, but the effect of isotopic substitution on free energies must also vastly differ in them. As a natural corollary to this prerequisite, in one phase the isotopic pair must exist in a strongly bonded state whereas in the other loose bonding. M/Hg is such a phase in which metal is loosely bounded with mercury. Further, dependent upon product and waste quality (i.e. X<sub>p</sub> and X<sub>w</sub>) and rate of production (i.e. P) and realising certain limitation such as practicable amalgam concentration etc. mercury requires to be pumped at high rate in the electrolyser (viz. ~ 200 lit./hr.) to produce M/Hg and flow it down column, at certain minimum rate (i.e. L) arrived at from cascade theory. From these, the reasons for selecting metal amalgam and large-scale use of mercury become obvious.

The operation of the pilot plant based on this process for the production of desired enriched material, therefore, leads to the contamination of the plant atmosphere with mercury vapour, and at such a site, finite exposure risk to mercury vapour exists for the personnel at work. In the present investigation an attempt is made to develop and delineate patterns for the spread of mercury vapour within engineering hall no. 5, due to pilot operations. For this purpose, the entire hall been imaginarily divided into six different and the spread patterns have traced out through the set of readings for airborne mercury levels taken over a period of about four month for each category. A mercury vapor analyser was used to monitor the mercury levels (Fig. 37). From this scanning-study we identify sites of high pollution and exposure risk to the personnel and could take prompt remedial actions wherever and whenever and necessary to maintain mercury levels under control. It has further brought forth emphatically the need to implement certain modification in the hall and its exhaust system to effectively reduce

exposure risk. A rough assessment of loss of mercury to surrounding through exhaust surrounding through exhaust and drainage routes is also made to evaluate its impact on the environment. In the introductory part, an overview of various aspects of mercury from pre-historic to modern period has also been purposely presented to appreciate its harmful and beneficial potentials. This, coupled with the present surveillance work has helped identify areas of high exposure risk and create greater awareness among the staffers to adopt right safely practice to be followed to minimized exposure risk while dealing with mercury on such a large scale.



**Fig. 37: Mercury Vapor Analyzer.**

**Sponsored Projects/ Patents/ Publications/ Thesis:**

- a) P.S. Kulkarni, et al., "Spread-Patterns-Development-Studies on Air Borne Mercury Levels at Various Sites in Engineering Hall No. 5, Due to Operational Activities of The Pilot Plant", *BARC Classified Report No./2002/R/003*.