Technologies for Sustainable and Green Solutions for Chemical Industry

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The drive towards sustainability in the chemical industry has to be taken up comprehensively from the start of the supply chain, to the manufacturing processes, the product characteristics and to its end use and disposal.

Revisiting existing processes and products and greening them is a very important step towards sustainability.

There are several things that can be done from process intensification to developing new catalysts, novel engineering to improved equipment design.

This article provides examples of four such developments, one for chemical reactions (Bio-catalysis/ Bio-transformations), one for a novel reactor which is on the verge of being commercialized (Downflow Gas Contactor) and two for downstream processing for various applications (Cavitation and Chromatographic Separation). In each case the background of the technology, it's industrial applications and couple of case studies are provided.

The concept of sustainable development has gained global importance in all industries in the last decade. Chemical industry is embracing sustainable approach to improve productivity and reduce waste generated:

a) by improving selectivity, yield and production through process intensification in chemical reactions;
b) through use of appropriate reactor design with improved agitation and heat exchange, whereby co-products and by-products are reduced; thereby reducing waste generated; and
c) by adopting new downstream processes to improve yield, produce better & desired quality products with physical and chemical characteristics and make the process continuous.

Further, with the use of appropriate catalyst and reactor design, companies are trying to reduce or eliminate solvents used in the reactions and carry out reactions at lower temperatures and pressures. There are several new technologies and reactor designs which have evolved or are under development; some of which have been commercialized successfully.

Biocatalysis/ Biotransformation

Enzymes are an important part of various industries due to their unique and favorable proper-

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ties. Development of industrial enzymes has depended heavily on the use of microbial sources, which can be produced economically by fermentation and inexpensive media. Starting 1970s, microbial enzymes replaced many plant and animal enzymes; and are now being used in many industries including food, detergents, textiles, leather, pulp and paper, diagnostics, therapy, and chemical synthesis. The development of recombinant DNA technology had major effect on production levels of enzymes as their genes were transferred from native species into industrial strains. Over 50% of the enzyme available in the market are produced by recombinant technology. In many cases, enzymes are being used to carry out chemical conversions that were performed by organic synthesis route earlier. Accompanying this trend is the use of whole cells to carry out bioconversions, which have become important to industry especially because of the demand for specificity for a product.

With significant progress on biotech area, and with limited oil/ coal resources, there is a push to develop bio-economy by creating integrated biorefineries, based on natural agricultural resources, which serve to produce sustainable biochemicals from flexible feedstocks. Biomaterials and biopolymers from renewable sources have been commercialized in last decade, which have established market now helping to lower the carbon footprint. Biorefineries will deploy innovative, sustainable technologies to complement the traditional energy, chemical, and plastics industries. Second-generation biofuels from cellulosics is now a reality. Research is focusing on advanced biofuels which would give rise to the possibility of more stable molecules having improved performance properties beyond bioethanol. Algae-based fuel technology is advancing rapidly toward commercial-scale viability. Commercial production of algae-based fuels will greatly enhance global energy and environmental security.

Enzyme catalyzed reaction plays major role to improve the productivity with greater selectivity. Many new APIs are based on biotech route. Amongst global top 20 APIs, at least 10-12 are bio-pharmaceuticals. Besides this industrial chemicals and polymers have been commercialized in the last decade; and many more are under development. Some of the commercially successful processes based on bio-catalysis/ biotransformations are:

1) Eastman Chemicals, USA have used immobilized lipases to produce esters for personal care and cosmetics application.
2) Purac-BASF and DSM-Rocquette have set up commercial plants for succinic acid using biotech route.
3) ADM, USA has used enzymes to produce trans fats and oils for foods.
4) Merck, USA partnered with Codexis, USA to use enzyme to reduce number of steps in synthesis of blockbuster anti-diabetic drug Sitagliptin. Overall yield increased by 10%, productivity improved by 50% and reduced waste by 20%
5) Pfizer used enzymes in Pregabalin synthesis leading to higher throughput, significant reduction in waste (by 30-40%) and reduced energy usage (by 80%).

Some of the advantages of bio-catalysis/ bio-transformations are:

- Milder reaction conditions (up to 60°C and atmospheric pressure)
- High selectivity (stereo/ region/ chemical)
- Increased productivity (shorter route of synthesis)
- Higher purity product (low/ no impurities)
- Lower cost of downstream processing (simpler purification, lesser impurities, lower solvent usage)
- Can be immobilized and reused

There are at least 150 biocatalytic/ biotransformation processes currently in commercial use in chemical and pharma industry. New scientific developments will facilitate tailoring of enzyme properties to increase that number significantly in future.

Some of the commercially used enzymes are shown in the table 1.

Case Studies:

1) Specialty ester used in food & polymer industry- Conventional process is carried out using acid catalyst at 80-100°C. The product obtained has mono-, di- and tri-esters. Using immobilized enzyme, the reaction is carried out at 40°C and produces ester with mainly mono- and limited di-ester only, which is desirable. The process can be operated in continuous mode.
2) Specialty ester used in polymer application- Conventional process is carried out by trans-esterification at around 225°C, producing some by-products. By using a bio-catalyst, the ester was produced at 45-50°C with more than 95% conversion in 5 hrs.

Downflow Gas Contactor (DGC)

There are significant developments in the last 2 decades in developing new reactors with better mass

Table 1: Types of enzymes

Enzyme Class	Reactions	Applications
Oxidoreductase	• C=O and C=C reduction • Reductive amination of C=O • Oxidation of C-H,C=C, C-N and	• Atorvastatin intermediate • Montelukast
Transferase	Transfer of functional groups such as amino, Acyl, phosphoryl, methyl, glycosyl, nitro & sulphur groups	• Sitagliptin • Cyclodextrin from starch
Hydrolase	Hydrolysis of esters, amides, lactones, lactams, epoxides, nitriles & reverse reactions	• Diltiaz intermediate • Esters
Lyase	Addition of small molecules to double bonds such as C=C, C=N and C=O	Statin Intermediates
Isomerase	Isomerisations such as racemizations, epimerizations & rearrangement reactions	HFCS from glucose

transfer, agitation, short contact time etc. Some of the new reactors developed in the last 2 decades include micro reactors, static mixers, microwave-assisted, cavitation based (using ultrasound and hydrodynamic cavitation), spinning disk to name a few, micro reactor is now being used commercially and widely.

Downflow Gas Contactor reactor is one of the most efficient mass transfer devices for contacting liquids and gases. It was developed at Birmingham University in 1990s and subsequently by WRK Design and Services Ltd. from 2002. It has evolved from a novel concept of contacting a liquid continuum and a dispersed phase. An intense shearing of the dispersed phase is induced with a minimum expenditure of energy over that required for motive power. Where the dispersed phase is a gas or another liquid, an enormous interfacial area is generated in a small containment volume. The interface is subjected to rapid surface renewal through repeated rupture and coalescence, resulting in intense mixing and highly efficient mass transfer. High interfacial areas are produced by exploiting a controlled hydrodynamic flow regime and do not require mechanical aids such as stirrers or baffles. In the case of DGC, not only can the performance be improved but operational and capital costs can be substantially reduced.

DGC is a downflow co-current device and consists of a cylindrical section with a specially designed orifice/ inlet at its entry section (at the top), allowing both liquid and gas inputs into the reactor (see Fig 1). For few specific applications, an additional inverted conical section may be provided after the cylindrical section for improved performance. Gas is concurrently fed into the incoming liquid stream immediately prior to the column inlet through the Specially Designed Inlet (SDI), which is the heart of this reactor technology.

DGC dimensions and configuration depend on the application and operating conditions. As the continuous phase expands in to the column, part of the kinetic energy imparted to the fluid on its passage through the SDI is used in the formation of interfacial area. Intense turbulence and shear at the interface results inefficient gas-liquid mixing and allows mass transfer operations to approach equilibrium in very short contact times. Some of the advantages of DGC compared with other contacting devices/ reactors are highlighted in Fig 2 and table 2.

The inherent simple design and operation of DGC offers specific advantages over other conventional contactors/ reactors, as listed below:

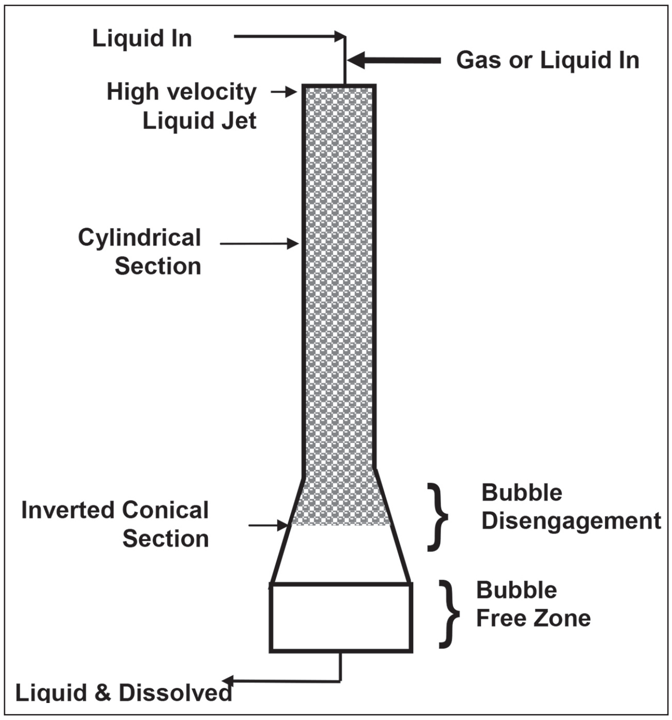

Fig 1- DGC design

- Lower power consumption.
- Smaller operating volume.
- 100% Gas utilization and >95% approach to equilibrium in short contact time.
- High and good control of interfacial area (1000 –6000 m^2/m^3), allows for improved reaction rates and reaction specificity.
- No internal moving parts like stirrer and hence lower operating costs.
- Higher gas hold-up (40-50%)
- Easy scale-up without loss in efficiency.

Table 2: Comparison of Operating Characteristics of DGC vs. Common Gas-Liquid Contactors

Gas-Liquid Contactor	Specific Surface Area, as (cm-1)	Liquid Side Mass Transfer Coefficient, kL (cm/s)	Max Volumetric Mass Transfer Coefficient, kLa (s-1)
Packed Column (Counter current)	0.1 – 3.5	0.004 – 0.02	0.0004 – 0.07
Bubble Column (Agitated)	1 – 20	0.003 – 0.04	0.003 – 0.8
Membrane	15 – 70	0.02 – 0.06	0.3 – 4
Spray Column	0.1 – 4	0.007 – 0.015	0.0007 – 0.075
Venturi Ejector	1.6 – 25	0.05 – 0.10	0.08 – 2.5
DGC	10 – 60	NA	0.2 – 12

a = Surface Area / Reactor Volume, (cm^2/cm^3)

Industrial Applications

Many industries require gas/liquid contactor in a wide range of processes and some typical examples where DGC can be beneficial are: Absorption; Stripping; Flotation; Ozone Treatment; Micro-bubble generation; Oxidation; Hydrogenation; Heterogeneous Reactions; Effluent Treat-ment; Fermentation; Mineral Separation.

Three key areas of commercial importance for DGC are Effluent Treatment, Chemical Reactions and Biogas Upgradation (for CO_2 capture & removal). Based on our (WRK and STEP) experience from the trials carried out in these areas, we see following advantages in each of the areas over current reactors used and technologies practiced presently in the industry.

Biogas Upgradation/ CO_2 capture

1) **Environmentally-friendly and cheaper absorption solvent:** The solvent used (branded as ABSOLV) is water-based containing specific salts. Competing technologies use organic solvents, which are expensive and corrosive. Other technologies are based on expensive membranes or use zeolites with high pressure operation.
2) **Single solvent:** ABSOLV can capture and separate both CO_2 & H_2S present in biogas/ flue gas or petrochem stream, in a single stage. With other technologies, CO_2 and H_2S are separated in sequential process.
3) **Plant size:** Most of the current biogas upgrading-technologies have limitations & do not perform effectively below 100 m^3/hr. DGC technology can be effective even for a small plant of 5 to 10 m^3/hr.
4) **Process parameters:** Competing technologies require either high pressure or high temperature to separate CO_2. DGC is operated at 20 to 25°C and atmospheric pressure. It can also be operated at higher pressures, if required.
5) **Comparion with Competitive technologies:** Other technologies viz. pressure swing adsorption, amine absorption, water scrubbing, cryogenic and membrane separation, produce Biogas with 95 to 98% purity of methane- there is few % loss of methane. There in no major loss of methane in DGC based process, it can produce biogas with improved quality (99+% methane). CO_2 removal is around

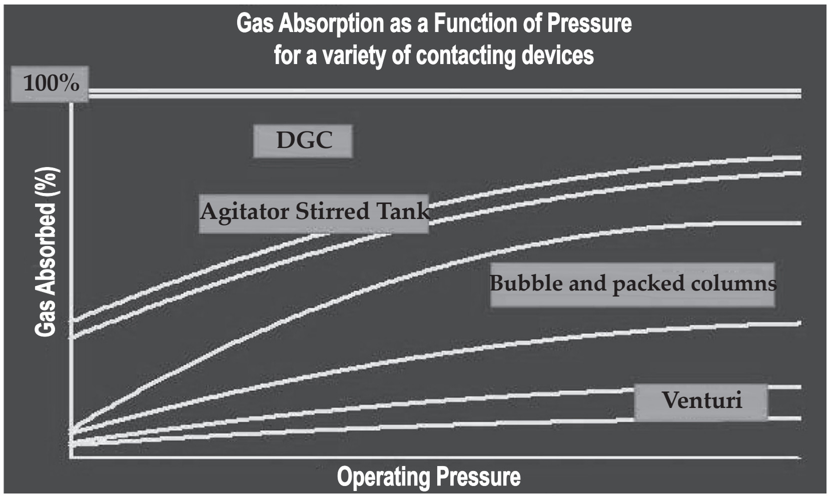

Fig 2. Comparison of DGC with other contacting reactors

99%, whereas competing technologies can remove around 95 to 98%. Capex for other technologies is higher than that for DGC. Typically a 500 m^3/hr biogas upgradation plant based on DGC reactor would cost at least 20% less than other technologies. The OPEX would also be lower.

6) Captured CO_2 can be recovered and utilised.

Effluent Treatment

1) It can be used for reducing COD of effluent containing a wide range of pollutants, and for land-filled leachates treatment using air, H_2O_2 & UV combination.
2) Works well on recalcitrant chemicals and chemicals, which are difficult to degrade (non-biodegradable)
3) The contact time required to reduce COD to specific level can be significantly lower than biological treatment; and the area for the plant will be much smaller.
4) DGC can be used as a stand-alone process or in combination with biological treatment in existing set-up of a company.

Chemical Reactions

1) **Faster reaction:** The reaction will progress at a much faster rate in DGC than in conventional reactors. This will benefit in terms of productivity and operation cost.
2) **Lower raw materials usage:** Use of catalysts, solvents and excess raw materials, used in a process could be reduced due to high mass transfer & reaction rates in DGC
3) **Higher conversion and selectivity:** Conversion and selectivity to main product could significantly improve, thereby reducing by-product and waste formation.
4) **Continuous process:** Reaction can be carried out in continuous process, thereby improving the productivity and reducing utilities used.

Case Studies

1) Effluent Treatment

We have carried out effluent treatment for range of industrial effluents since early 2016. Some of the effluent streams had phenols, and nitrogen containing chemicals. We have achieved up to 80% COD reduction in 4 to 8 hours using either air only or combination of air-H_2O_2 and UV. Table 3, shows results of 4 effluent streams treated on DGC set-up available with us. It can been seen from the results that DGC not only reduces the COD&BOD but also TDS, TSS and Ammonical Nitrogen in some of the cases.

2) P-Cresol Oxidation to p-Hydroxy Benzaldehyde

Catalytic oxidation of p-cresol was performed in DGC reactor using pure oxygen. The reaction was carried out at 70^oC. Reaction rate was limited by the cooling capability of the reactor setup due to exothermicity of the reaction. Despite this, the p-cresol conversion was found to be > 90% (vs 75 to 80% for conventional reactor) with selectivity of around 95% for p-HBA.

3) Biodiesel reaction

Transesterification reaction is carried out with the lowest ratios of methanol :oil and low catalyst [NaOH] concentrations. Different types of oils- edible or non-edible as well as waste cooking oil were used. The reaction was undertaken at ambient temperature. The reaction and overall contact times are low (3 to 5 mins), and ester or biodiesel yields are high [95%-98%]. Methanol utilisation is greater than 98% and there is low concentration of residual methanol in the biodiesel produced. Due to low concentrations of methanol and catalyst, there is easy settling and quick phase separation of the glycerol produced. DGC reactor can also be used as a settling and separation vessel with quick turnaround times. The biodiesel produced can meet the required specifications.

Table 3- Results of treatment of effluent stream using DGC

Effluent Stream	Results	Residence Time (Min)
Commodity/ specialty chemicals	COD: Reduced by 33 to 53%	45
Sugar Mill –Sugar condensate	COD reduced by 80%	75
Common effluent treatment plant (CETP)	COD- ~ 55-80% with air, TSS-38 to 48%,TDS- 30-50%, BOD-40%	65 to 100
Alcohols containing stream	COD-35%, BOD-35%. Ammonical Nitrogen- 100 ppm to <1ppm using air & H_2O_2/ UV	35

Cavitation

Cavitation is one of the emerging technologies being practiced in chemical industry for process intensification over conventional technologies. Cavitation phenomenon is caused due to formation and implosion of cavities in a liquid resulting into very high energies. It usually occurs when liquid is subjected to rapid changes

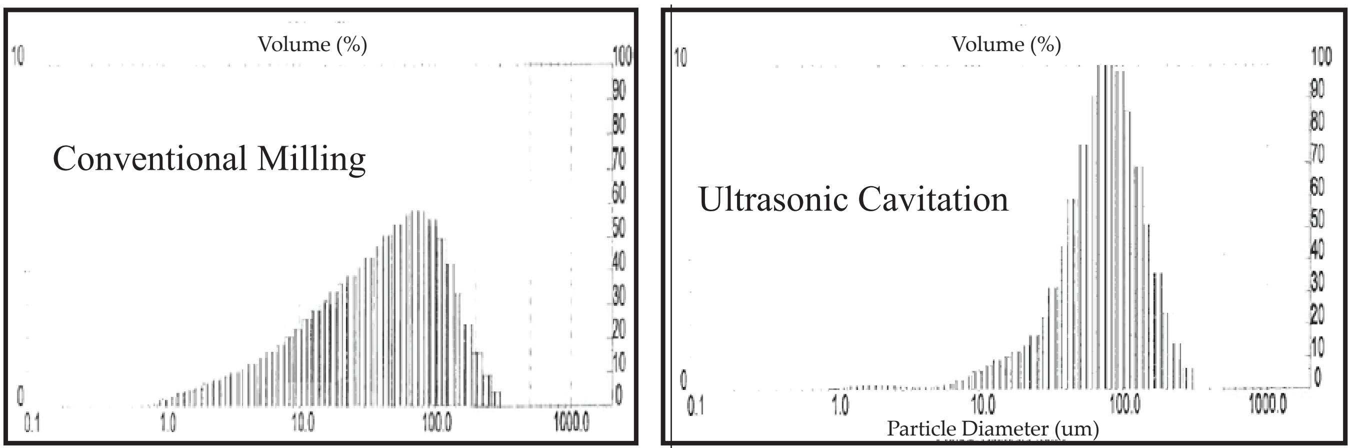

Fig 3- PSD using conventional milling vs. ultrasonic cavitation

of pressure that cause the formation of cavities when the pressure is relatively low. Cavitation is achieved by two methods viz. acoustic (ultrasound) and hydrodynamic (with orifice or venturi). Depending on end application, appropriate cavitation technique is applied.

Acoustic cavitation is caused by pressure variation in the liquid due to sound waves usually ultrasound (16 kHz-100MHz). It is produced either by ultrasonic transducers in which the medium is in indirect contact with the ultrasound device or by ultrasonic horn in which the reactants are in direct contact with ultrasound device. Ultrasonic cavitation can be applied to flow cell, wherein transducers are mounted on the two opposite sides of the vessel or around a pipe. Flow cells can be operated in batch and continuous mode.

In acoustic cavitation, which is widely used, the pressure variation is caused by geometrical obstacle resulting in change in the pressure and kinetic energy. Hydrodynamic cavitation is generated using orifice or venturi.

Applications:

Ultrasonic Cavitation

- Ultrasonic cavitation has been used on commercial scale for crystallization of pharma drugs. It can help in producing the desired polymorph of an API. Prosonix, UK has been working closely with few pharma companies to use ultrasonic crystallization to produce selective polymorphs of APIs. Some of the processes have been commerciliased,
- It is used in pharmaceutical industry to produce nano emulsions and suspensions incorporated in formulated drugs.
- Variety of nutraceuticals, organic acid, proteins can be extracted from natural products with cavitation using ultrasound. Cavitation effect causes the rupture of the cells/ solid matrix resulting in the release of the compound of therapeutic value.
- It has been used in chemical synthesis in homogeneous reactions viz. oxidation. In heterogeneous reaction medium, cavitation plays a major role to increase the mass transfer in the catalytic reaction.

Hydrodynamic Cavitation

- It can be used for effluent treatment to reduce COD. The contaminants in water are destroyed due to localized high concentration of oxidizing agents and free OH radicals generated due to higher magnitude of localized temperature and pressure. These oxidizing species results in destruction of the contaminants.
- It is commercially used in treatment of cooling water in cooling towers. Using specific venturi design, the cavitation generated helps in destroying the bacteria/ fungi and reduce/ eliminate scaling/ fouling of the heat exchanger. This helps to eliminate use of biocides and descaling agents. Water blowdown reduction upto 30% have been reported on commercial scale. VRTX, USA has successfully commercialised this technology and has set up several plants for cooling water treatment in USA.
- It can be used in synthesis of nano crystalline material, nano emulsion production, in preparation of high quality of quartz sand etc.

Case studies

1) **Crystallization and particle size distribution control of specialty chemical.** Crystallization of a specialty chemical was carried out at pilot level using a flow cell. The main objective of using cavitation was to carry out crystallization and milling in sin-

gle stage and control particle size distribution. With appropriate methodology of applying ultrasound, desired PSD was achieved. From the fig 3, it can be seen the PSD using cavitation can be controlled within narrower range compared to conventional crystallization + milling process. Using this technology, 3-5% fines and oversize particles produced by conventional crystallization + milling, was reduced.

2) **Milling:** Conventional process required around 10-11 passes of milling, and at least 3-4 days to achieve desired quality of a dye. With ultrasound treatment for couple of hours in a selective way helped in reducing number of passes, and milling time to around 1 day.

3) **Cooling water treatment:** Conventional process uses biocides and descaling agents to eliminate/ control bacteria and fungal growth, and control scale formation in cooling tower. With hydrodynamic cavitation, bacteria/ fungal growth was stopped without addition of biocides. Scaling and temperature gradient across tubes build-up was delayed by few weeks. Also, the scale formed were easily removed unlike hard scales formed in conventional process. Effluent treatment cost was also reduced due to elimination of chemical usage.

D) Chromatographic Separation

Chromatographic separation is an increasingly important separation technique in fine chemical, pharmaceutical, nutraceutical and biotech industries. Over the years, the operation of the chromatographic process in these industries has undergone many developments and improvements. Batch processes are converted into continuous for ease of operation and control of the product quality. In the past mainly silica, alumina, zeolites or ion exchange resins were used. In the last 2 decades manufacturers have developed new adsorbents with specific properties and characteristics to separate/ purify specialty chemicals. While the single column is still popular in preparative chromatography, multi-column processes, such as simulated moving bed (SMB) chromatography or multiple columns, are now becoming increasingly popular in industrial-scale chromatography as a continuous means to produce large amounts of highly purified products. Based on available info and some lab trials, one can determine which is the most suitable chromatographic process for a given separation, given the vast range of adsorbents and ion exchange resins available now. Chromatography is one of the most frequently used techniques for purification of proteins, peptides, nucleic acids and other charged biomolecules, offering high resolution and separations with high loading capacity. The technique is capable of separating molecular species that have only minor differences in their charge properties, for example two proteins differing by one charged amino acid. These features make ion-exchange resins and adsorbents well suited for capture, intermediate purification or polishing steps in a purification protocol.

Adsorption - separation technology is also widely used for purification of intermediates, and removal of metals. Silica, ion exchange resins and polymeric adsorbents are used for such applications. Though adsorption-separation is reported for effluent treatment, it is used commercially in only limited applications viz. metal removal, phenol recovery to name a few. The advantage of this technology is that it can selectively remove a chemical or metal. However, other similar chemicals present in the effluent stream may also get adsorbed and separated. This process is typically operated at room temperature and atmospheric pressure in a column of adsorbent. The adsorbed chemical/ metal is eluted with a solvent at the end of an adsorption cycle.

The adsorbent is renewed by washing it with a solvent. The challenge in some cases is complete regeneration of the adsorbent for reuse. At times the adsorption capacity may gradually drop due to strong adsorption of some impurities. In such a case, the adsorbent may have to be regenerated by backwashing the column with an appropriate solvent. Generally, these adsorbents can last from >100 cycles up to 500 cycles.

Chromatographic separation has various advantages over other separation-purification technologies viz. improved/ higher yield, better quality of product, impurity can be removed selectively and continuous process.

Case Studies

- **Purification of a specialty chemical:** The specialty chemical had yellowish color due to impurities present. Conventional method involved treating it with activated carbon, which would lead to traces of black particle (activated carbon) in the product. Using synthetic adsorbent, not only the color of the product was improved but also the purity of 99.9% was achieved as against 99.5+% with activated carbon process. The resin was tested for 5 cycles of use and regeneration without loss of activity.
- **Recovery of metals:** An effluent stream from a reaction process contained metal which was being discharged into ETP. We used a fluidized moving bed column with ion exchange resin for adsorption of the metal from feed (effluent stream). The metal was in chloride form. Elutant used was aq. HCl. Recovery of the metal was 99.9%.
- **Chemicals recovery from waste:** Recovery of raw material & solvents used in chemical reactions was successfully and selectively done from effluent streams by adsorption using specialty adsorbents. The quantity of chemical to be adsorbed differed from 0,5 to 25% in the effluent stream. Results of 3 different streams containing different chemicals are given in table 4.

Table 4: Effluent treatment and recovery of chemical case studies

Chemicals	Recovery	Eluent
Dimethyl Formamide	~90%	Methanol
Methylene dichloride	~98%	Methanol
Aniline	~98%	Methanol

Conclusion

Many of these technologies can assist and help in not only improving the productivity of a process but also improve the quality of product produced and reduce the waste generated. There is always resistance to change, to adopt new and improved technologies particualrly with production/technical personnel, which need to be overcome.

Editor's Note

STEP has partnered with WRK Design and Services Ltd., UK to promote a novel reactor called Downflow Gas Contactor (DGC). Now in the process of successfully commercializing some of the case studies, which will benefit customers. Especially in DGC reactor, they currently in advanced stage of discussion with Indian companies to implement it for effluent treatment; and with overseas companies for setting up commercial CO_2 removal/ biogas upgradation plant.