Sustainable Approach for Effluent Treatment in Chemical Industry

Dhiraj Mishra, Mitesh Gaikwad, Ms Sayali Dhanawade, Dr M G Palekar

Abstract

Sustainable Technosolutions for Environmental Protection (STEP) Pvt. Ltd. has worked in process audit; water and wastewater audit/ management/ treatment and infrastructure projects. They work concepts using new generation of flocculants, and technologies currently available to meet the sustainability objective. The article elaborates on these concepts with case studies and techno-economic benefits they provide.

Sustainable Technosolutions for Environmental Protection (STEP) Pvt. Ltd. was established in 2010. Since the last 6 years STEP has worked in process audit; water and wastewater audit/ management/ treatment and infrastructure projects. They undertake Effluent Treatment Plant (ETP) design for new facility and upgradation of existing ETP.

They work concepts using new generation of flocculants, and technologies currently available to meet the sustainability objective. Three of the concepts are listed below:

1) New generation of flocculants to reduce COD/ TSS
2) Adsorption- separation technology to recover and reuse a chemical from effluent
3) Novel Gas-Liquid reactor, Downflow Gas Contactor (DGC) for effluent treatment

These concepts have shown encouraging results in lab and pilot plant. Basic information on each area along with case studies is presented below. We have also provided techno-economic benefits for these case studies to emphasize its advantages.

A) New Generation of flocculants to reduce COD/ TSS:

Polyelectrolytes are water soluble polymer carrying ionic charge along the polymer chain. Depending upon the charge, these polymers are anionic or cationic. They are available in a wide range of molecular weights and charge densities. They have a wide range of applications from water purification, wastewater treatment, colour removal etc.

Flocculants are a type of polyelectrolytes. A flocculant is essentially a solid liquid separating agent. Use of new generation flocculants for wastewater treatment is a sustainable approach because the chemical consumption is less, and chemical oxygen demand (COD) & total suspended solid (TSS) removal efficiency is more, at a lower cost.

Treatability studies were performed using the floc-

Authors

Dhiraj Mishra is a B.E. (Biotech Engg) (Diploma in Electronics Engg) is working with STEP since Aug 2015 as Environmental Engineer.

Mitesh Gaikwad is BSc (Chemistry) (PG diploma in Environmental Pollution Control Technology) is working with STEP since Feb 2015 as Environmental Executive.

Ms Sayali Dhanawade is BSc (Chemistry) (PG diploma in Environmental Pollution Control Technology) is working with STEP since Nov 2014 as Environmental Executive.

Dr M G Palekar is B. Chem. Engg., PhD (Tech) is Head- Strategy & Technology at STEP since June 2014. He has a Post-Doctoral research experience from Gent University, Belgium. He has worked in various Indian and MNCs in R&D, Marketing and managing the business, and has 26 years of experience in Industry.

culants of an MNC. Jar test was carried out using different flocculants based on characteristics of the effluent. TSS and COD of the effluent were checked at the end of the treatment.

Case study I

Chemical Company

In Case I, effluent treatment was done of a commodity & specialty chemicals manufacturing company. The effluent was treated physico-chemically, followed by biological and tertiary treatment. In spite of physico-chemical treatment, TSS got carried over in biological treatment that affected treatment efficiency.

Jar test studies were performed using 3 flocculants on effluent from equalization tank of ETP. The pH of effluent was adjusted to 7 by addition of lime. Results of the trials are presented in Table 1.

The results indicate that with two of the new flocculants (B & C), TSS and COD were lower by ~50% and 15 to 40% respectively vs. current flocculant used by the company. The best results were achieved with B at pH 7 and 0.1% concentration, when TSS was found to be lower by 55% and COD by 40% vs. currently used flocculant.

Cost estimate

The cost comparison based on above results for best flocculant with the current used by the company is given in Table 2.

Based on these results further optimization work was done to arrive at an optimum dose. Though the cost was marginally lower, based on the advantage of higher TSS and COD reduction, which will help in the biological treatment cost, the company has shifted to flocculant B. This will help in biological treatment.

Case study II

Specialty Chemical company

In this case effluent treatment was tested on ingredients for personal care & food manufacturing company. The effluent was treated physico-chemically, followed by biological and tertiary treatments.

Jar test studies were carried out on effluent from neutralization tank using a specific flocculant. Results are presented in Table 3.

With D at pH 7 and 0.05% concentration, TSS and COD were lower by 50% and 10% vs. current flocculant used. The amount of dosing required are considerably less (8 mg/l) than the present polyelectrolyte dosages (42 mg/l).

Cost estimate

Monthly consumption cost of current flocculant vs. D is given in Table 4.

Thus using D, the monthly cost of flocculant would reduce by almost 50% with advantage of increased removal of TSS and COD.

Conclusion

Selection of correct flocculant can help in improved TSS and COD removal in primary treatment, thereby improving the efficiency of biological treatment, and possibly reduction in cost of primary treatment.

B) Adsorption- separation to recover and reuse a chemical from effluent

Adsorption- separation technology is widely used for purification of intermediates & APIs in pharmaceutical industry, biochemicals & natural products, and for removal of metal. 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/ metal. However, if some other similar chemicals may also get adsorbed & separated. The adsorption & separation is typically

Table 1

Flocculants used	% concentration	Dosage (mg/L)	pH	TSS	COD	% TSS removal	% COD removal
Effluent sample	-	-	7	1980	3525	-	-
Current flocculant	-	6.92	7	412	2223	79	37
A	0.1	2	6.37	403	1428	80	60
B	0.1	5	6.89	180	1344	91	62
C	0.05	1	6.9	170	1855	91	47

Table 2

Flocculant	Price (Rs/kg)	Chemical Consumption (kg/day)	Chemical Consumption (kg/month)	Cost (Rs/month)
Current flocculant	225	0.45	13.5	3038
B	306	0.325	9.75	2984

achieved at room temperature and 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 another 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 last from >100 cycles up to 500 cycles.

For application in effluent treatment the authors have focused on removal of difficult biodegradable or non-biodegradable chemicals from effluent stream. This may also contribute significantly to COD or may need specific treatment (anoxic). The authors worked on nitrogen containing chemicals, phenols, chlorinated solvents. With selective adsorption of the chemical, it could be recovered and possibly reused in the process, if it is a raw material. Alternately if it is a finished product, the recovered product could be purified & sold. This will help the company to reduce the cost of production as well as effluent treatment cost.

We first study possible chemicals in the effluent stream. Then we scan range of adsorbents available with help of our overseas Principal, and select appropriate adsorbent for the trials, based on characteristics of the effluent & chemical to be adsorbed. The studies are carried out in two stages- first in batch process for proof of concept to confirm adsorption of the chemical and recovery. Once the 'proof of concept' is established then we go for continuous process using column chromatography to optimise the process.

Adsorption- separation technology is widely used for purification of intermediates & APIs in pharmaceutical industry, biochemicals & natural products, and for removal of metal. Silica, ion exchange resins and polymeric adsorbents are used for such applications.

We have now worked on few such projects, results of some of these are presented below. One important aspect of these studies is that, we have used the effluent stream in some of the studies on 'as is' basis without neutralization.

Case study 1

Pharmaceutical company - Dimethyl Formamide recovery

This company used Dimethyl Formamide (DMF) as solvent in one of their API process. The company had tried to recover it by distillation but were not successful due to temperature sensitivity of DMF. Further since DMF is nitrogen containing chemical; they had problems to treat it in their ETP. Hence, they were segregating the effluent containing DMF and sending it for incineration at a third-party, which is an expensive solution.

We carried out proof of concept studies using two different adsorbents and found both to be suitable. In lab trials, we successfully removed ~90% DMF from effluent stream, and also recovered DMF using methanol as eluent. COD and Ammoniacal nitrogen were reduced by 20 to 35% respectively in the effluent, and the yellowish colour of effluent was removed completely.

Quantity of effluent stream generated in 5 batches of the intermediate was 4 KL/ month with 25% DMF. We considered DMF recovery in 20 batches. Based on the proof of concept results, estimate of adsorbent required was 1.5 T. Assuming 300 cycles of generation, the life of adsorbent would be ~15 months. With 90% recovery of DMF & considering 50% market price of recovered DMF, we estimated that the DMF recovered in 15 months + cost saving on incineration, will more than compensate the cost of adsorbent + operating cost of the system.

Though the process was found to be economically viable, the company declined to proceed further due to

Table 3

Flocculant used	% concentration	Dosage (mg/L)	pH	TSS	COD	% TSS removal	% COD removal
Raw effluent sample	-	-	7	46500	3871	-	-
Current flocculant	0.05	42	7	38400	3414	17	11.81
D	0.05	8	7	19900	3089	57	20

Table 4

Flocculants	Price (Rs/kg)	Chemical Consumption (kg/day)	Chemical Consumption (kg/month)	Cost (Rs/ month)
Current flocculant	120	4.2	126	15120
D	279	0.8	24	6696

high cost of the adsorbent.

Case study 2

Pharmaceutical company (Methylene dichloride recovery)

This pharma company uses methylene di-chloride (MDC) as a solvent in one of the intermediates of an API. MDC is not easily biodegradable. Due to the presence of MDC they face problems to operate their biological treatment facility in ETP. MDC and chlorides beyond 500 ppm deactivates the sludge in biological reactor.

We worked on adsorption and recovery of MDC with 2 adsorbents. One of the adsorbents adsorbed ~98% MDC from effluent stream & recovered it using Methanol as eluent. The COD of the effluent reduced by 17%. Colour of the effluent also improved.

This company is exploring further to optimize the process in lab using continuous column chromatography.

Case study 3

Chemical company (Aniline recovery)

This chemical company manufactures specialty intermediates, one of them is based on aniline. The unreacted aniline in the process ends up in effluent. The effluent stream is 2 to 3 kilo litres per day (KLD) with 0.5 to 0.8% aniline, while rest of the effluent from the factory is around 50-60 KLD, with COD of 5000 to 6000 ppm. With aniline stream addition to the main effluent stream, COD increases significantly and being a nitrogen containing chemical biological treatment efficiency is affected. The total quantity of aniline in effluent is in the range of 12 to 20 kg/day.

Using two different polymeric adsorbents, we successfully separated & recovered around 98% Aniline. Methanol was used as eluent, which was distilled out to recover aniline. We evaluated regeneration and reuse of the adsorbent for 5 cycles and found that there was a drop in capacity after 5 cycles.

Quantity of effluent stream generated is 2.5 KL per day with 0.7% average aniline concentration. 20 batches of product are produced every month. For the aniline quantity in effluent 0.5 T adsorbent is required based on adsorption capacity estimated from lab trials. Assuming 300 cycles of generation, the life of adsorbent would be around 15 months. With 90% recovery of aniline & considering 50% market price of recovered aniline, we estimated that the aniline recovered in 15 months and cost saving on effluent treatment, separation & reuse of aniline will more than compensate the cost of the adsorbent + operating cost of the system.

The company has set up a pilot facility to evaluate the process for separation and recovery of aniline.

Conclusion

From the above case studies, we feel that in specific effluents which contain difficult biodegradable chemicals, it may be worthwhile to explore separation & recovery using adsorbent. This helps in not only recovery of raw material/ product but also in improved treatment of the remaining effluent as well as cost saving.

C) Novel Gas-Liquid reactor, Downflow Gas Contactor (DGC) for effluent treatment

DGC reactor is one of the most efficient mass transfer devices for contacting liquids and gases. 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 stirrer or baffles. In case of DGC, not only the performance can be improved but also operational costs and at times, capital costs can be substantially reduced per kg basis for commercial plants. (Fig 1)

DGC consists of a column, the dimensions and configuration of which depend on the application and operating conditions. The novel feature of the design is the downward co-current flow of the dispersed and continuous phases through a specially configured nozzle or orifice and entry zone at the top of the column. As the continuous phase expands into the column, part of the kinetic energy imparted to the fluid on its passage through the nozzle is used in the formation of interfacial area. The intense turbulence and shear at the interface results in efficient gas- liquid mixing and allows mass transfer operations to approach equilibrium in very short contact times.

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

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

DGC can be used for 3 key industrial applications:

1) Gas-Liquid and liquid-liquid chemical reactions like hydrogenation, chlorination, oxidation, amonolysis etc.,
2) Effluent treatment to reduce COD/ BOD and
3) Gas capture from gas mixture/ effluent gases e.g. CO_2 capture from biogas.

For last 2 years STEP is promoting DGC technology for above applications in India with help of our technology partner WRK Design & Services Ltd, UK. STEP has set up a pilot unit in collaboration with Snowtech Equipments Pvt. Ltd., Navi Mumbai. This unit is currently being used for effluent treatment of various industrial effluents, wherein air/ oxygen and H_2O_2 are used as an oxidising agent. In past 1 year, we have carried out trials on different industrial effluents. Effluent samples were tested for Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Dissolved Solids (TDS) and Total Suspended Solids (TSS). For most of the trials results, were positive with COD reduction of between 25% to 80% in 3 to 5 hours using mainly air or oxygen. In some of the trials, BOD reduction was up to 50%, TDS up to 30-40%. It is important to note that though COD reduction is done in 3 to 5 hours of operation, the effective residence time of the effluent in the reactor was typically between 45 to 100 minutes.

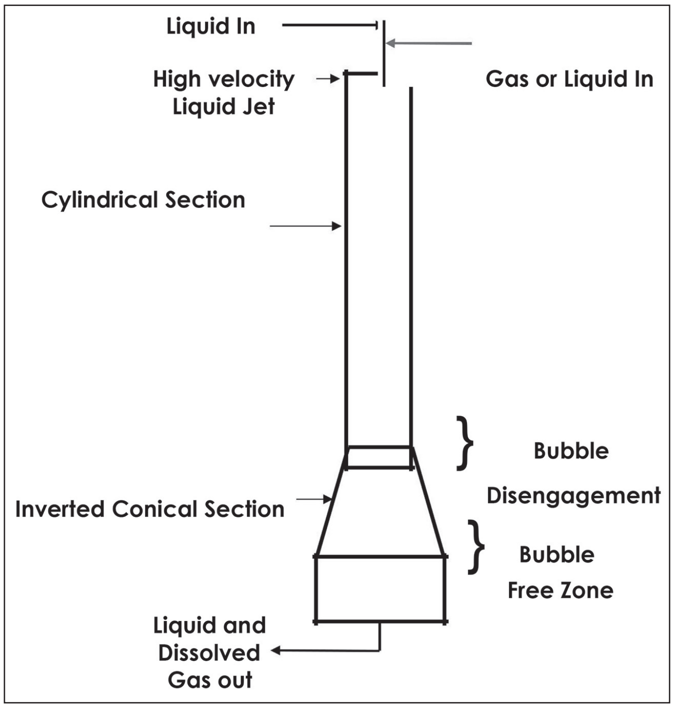

Fig 1

DGC reactor is one of the most efficient mass transfer devices for contacting liquids and gases. 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.

We feel that DGC can be used independently or in combination with existing biological treatment. The operating cost is estimated to be competitive with respect to biological treatment. We are presenting some of our case studies.

Case Study 1

Effluent was from a commodity and specialty chemical manufacturing plant. Three trials were conducted on DGC using effluent after primary clarifier. The operating parameters of all the three trials are marginally different. The reactor was operated for 4 hours and samples were collected from time to time. Two different types of inlets were used in these trials. The results obtained are presented in the Table 5.

As can be seen, COD reduced in all three trials by 33% to 53%. Though the trials were carried out for 4 hours the effective residence time of the effluent for treatment was around 45 mins.

Case study 2

Trial was conducted on DGC using sugar condensate effluent from a sugar mill. The trial was performed for 4.5 hours using air for oxidation. Samples were collected from time to time. The results of initial & final samples are given in Table 6.

80% COD was reduced in 4.5 hours, and the effective residence time of the effluent in DGC for this treatment was around 75 mins.

Case Study 3

This effluent was from a Common Effluent Treatment Plant (CETP). To ensure that the effluent is representative, 100 lts effluent after primary clarifier was collected every day over 10 days, and mixed to get a composite effluent. This composite effluent was used for the trials.

Two sets of trials were performed. First set of trials was carried out for proof of concept for 6 hours using two different inlets and air or oxygen. The key results of these trials are summarized below.

1) TSS reduced by 38 to 48% (from ~475 ppm).
2) TDS of effluent decreased by 8 to 20% (initial TDS ~12000 ppm). This feature of DGC is important as reverse osmosis and evaporation are the only simple methods to reduce TDS in effluent.
3) COD reduced by 24% to 55% with air or oxygen (Initial COD ~1800 ppm).
4) BOD decreased by around 40% (initial BOD ~800 ppm)

Second set of trials were performed 3 months after first set of trials. The trials were carried out for 8 hours using air. In these trials, COD reduced by 80+% (initial COD was 980 ppm) and TDS reduced by 50+% (initial TDS was 3400 ppm). The effective residence time for first trial was around 100 mins while in second set of trials it was 65 mins.

Based on these two sets of trials, it confirms that DGC has performed successfully for not only COD reduction but also for TDS reduction.

Table 5

Sample	Time (hrs)	pH	COD (ppm)	% COD removed
TRIAL-1				
1	0	7	4800	
2	1	7	3400	29.2
3	4	7	3000	37.5
TRIAL-2				
1	0	7	4600	
2	1	7	3800	17.4
3	3	7	3100	32.6
TRIAL-3				
1	0	7	6000	
2	1	7	2858	52.4
3	3	7	2800	53.3

Table 6

Sample	Time (hr)	pH	COD (ppm)	% COD removed
1	0	6.9	2160	-
4	4.5	6.9	432	80

Case Study 4

This effluent contained couple of alcohols. We used H_2O_2 and air as oxidizing agents in the trials. Two trials were taken with 2 different orifices for 4 hours each. For initial 2 hours only air was used as oxidizing agent. Addition of H_2O_2 was done only after two hours in both the trials. The key results are summarized below.

1) For the first 2 hours when only air was used, there was no reduction in COD.
2) After addition of H_2O_2 and with air, the COD reduced by 35% in both the trials.
3) BOD reduction was similar to COD by in both the trials (~ 35%).
4) Ammonical nitrogen reduced from 93 ppm to <1 ppm in both the trials. This is an interesting and positive aspect of H_2O_2 treatment for this effluent.

The effective residence time in these trials was around 35 mins.

Conclusion

Based on the above case studies, DGC seems to be an interesting option wherein the effluent treatment to reduce COD/ BOD could be done in very short time versus the conventional treatment. Further, in 3 of the cases only air was used asoxidizing agent for COD reduction. We feel that in many cases all the COD may not be effectively removed using DGC and some biological treatment may be needed after DGC to meet the effluent discharge norms. Additionally, the size of the DGC system will be smaller than a conventional biological treatment.

Thus using above described concepts, independently and in combination, companies can improve the effluent treatment efficiency, recover chemicals through adsorption-separation and improve the degradation of chemicals using DGC. This will help in reducing the effluent treatment cost and recycle of water after tertiary treatment, which will lead to sustainable approach.