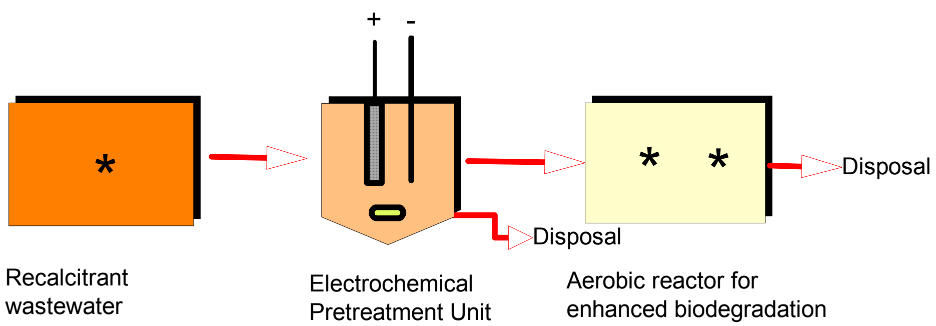
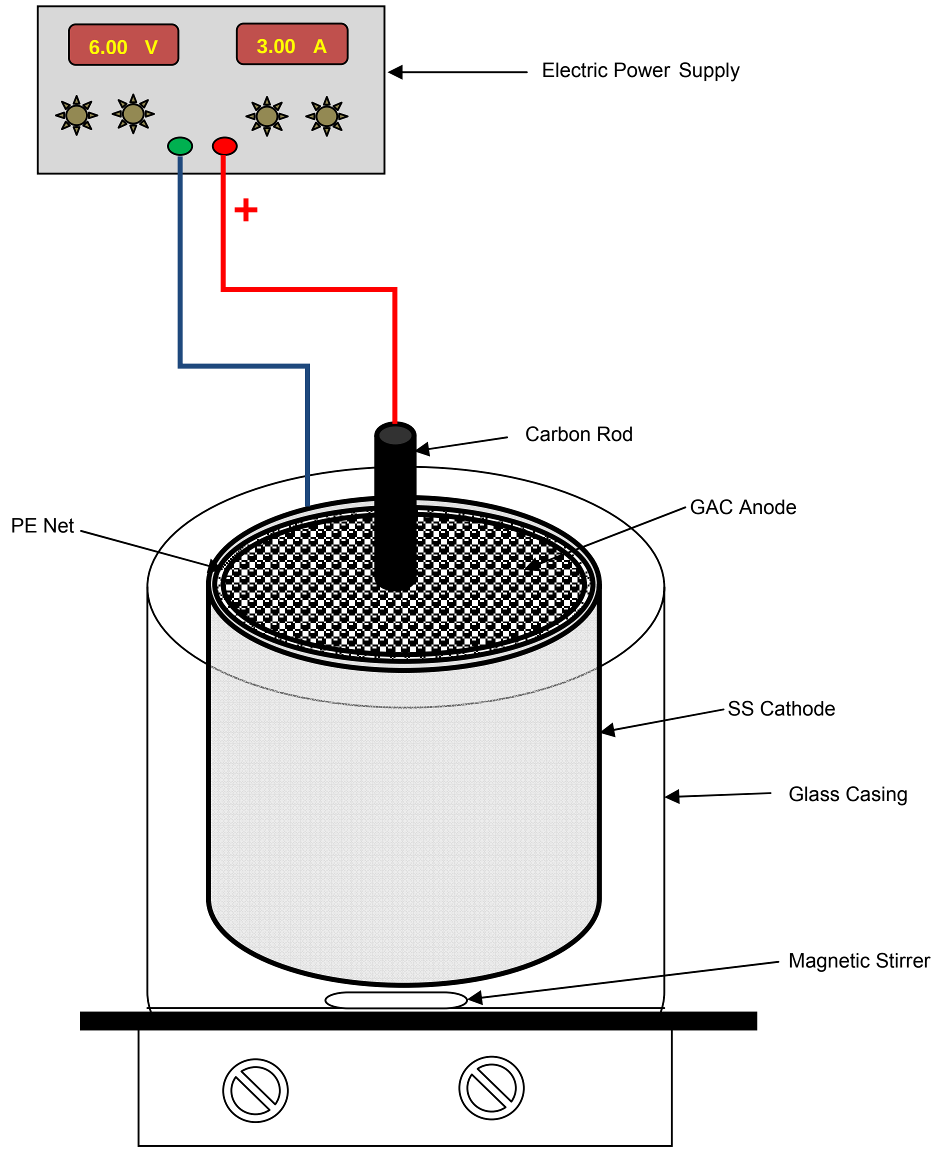
Processes / Know-How Developed

- **Development of high surface area three-dimensional electrodes using attractive C-materials for *in-situ* destruction or modification of organic pollutants (DST sponsored)**

NEERI undertook this project to develop high surface area three-dimensional electrodes to destroy non-biodegradable chemicals present in wastewater. Studies on the development of high surface area three-dimensional electrodes (3D-C), based on attractive high surface area carbon materials for anodic oxidation of organic pollutants, have been carried out. The 3D-C anodes were fabricated using C-materials, characterized electrochemically as well as morphologically and finally tested in a flow-through electrochemical reactor. Apart from some of the reactive dyes in simulated textile wastewater, real wastewater from different stages of conventional treatment plant was separately subjected to these studies and extent of bio-degradability induced was estimated. It was required to develop such anodes to achieve high efficiency and high throughput treatment of recalcitrant wastewater. This new method was developed to exploit high surface area C-materials for their attractive adsorptive function coupled to the anodic oxidation of recalcitrant organic compounds present in textile wastewater. Know-how was developed to fabricate 3-D carbon anodes with efficient current collection mechanism and their application to anodic oxidation. In CETPs where the performance of activated sludge process is unsatisfactory due to presence of reacalcitrant organic compounds, this know-how can be pilot tested as a pretreatment unit to increase performance of secondary aerated tank.



A schematic diagram of the treatment process



Flow through electrochemical reactor

- **TSB process for treatment of ammonia bearing process effluents from agrochemical industries**

Ammonia in industrial effluents, when present in high concentration along with high concentration of organics, upsets biological treatment processes. Conversely, biological nitrogen removal is also severely affected by the presence of organic compounds, especially VOCs, in an agrochemical industry. Usually, if industrial effluent contains high concentration of ammonia, a stripper is employed to strip off ammonia. However, due to ineffective operation of the stripper and also because of its poor maintenance, efficient removal of ammonia is not achievable. As a result, the downstream biological treatment process receives effluent containing high concentration of ammonia. Conventionally, the effluent treatment plants (ETPs) are not scientifically designed for biological treatment of ammonia. The biological processes are generally designed to remove BOD and COD. Hence, the presence of ammonia in high concentrations, along with organics poses problem in treatment, thereby reducing the process efficiency of the biological system designed. The reason is that the conventional activated sludge or extended aeration systems fail to provide the specific environmental conditions to the complex microbial populations needed for simultaneous removal of carbon and nitrogen.

In this direction, NEERI has developed a Two-Stage Biooxidation (TSB) process for removal of organics and ammonia from effluents having complex mixture of organics, VOCs, phenolic compounds, cyanide and ammonia. The TSB process is an outcome of NEERI's hands-on experience on environmental bioremediation including wastewater treatment through application of biochemical processes for removal of pollutants from wastewaters. Agrochemical industry is a 'red category' industry generating highly complex process effluent of environmental concern. The TSB process developed by NEERI can specifically cater to the problems that arise while biologically treating complex agrochemical effluent containing organics, VOCs, phenolic compounds, cyanide and ammonia.

The principle of the TSB process

The TSB process works on the principle of stage separation that avoids competition between two generic groups of microorganisms, namely the heterotrophs and autotrophs. The heterotrophs are the fast growing group of microorganisms that derive their food and energy from destruction of organic matters present in the effluent. While, the autotrophs are the slow growing groups of microorganisms that assimilate food from atmospheric CO_2 and derive energy from redox reactions involving inorganic compounds. Due to the basic difference between these two generic groups of microorganisms in acquiring carbon and energy, the heterotrophic group of bacteria always outgrows the slow growing autotrophic bacteria and also depletes essential nutrients that may be in limiting concentrations in the effluent. The TSB process ensures separation of autotrophic and heterotrophic bacterial population by time and space, thereby avoiding competition for oxygen and nutrients. The stage separation targets removal of specific pollutants in each stage which is otherwise not sustainable in single-stage conventional process.

About the TSB process

The TSB process involves a two-stage sequential batch reactor system. Each stage functions as a cyclic activated sludge process comprising filling, aeration, settling and decantation phases. A pretreatment step comprising ammonia stripping is recommended to achieve sustainable influent characteristics for the TSB process. The equalized effluent after pre-treatment through ammonia stripper flows into a tank where pH and other nutritional conditions (CNP ratio of 100:5:1) are adjusted for the downstream biological process. Once the desirable conditions for biological treatment are met, the effluent is pumped into stage I unit of TSB process at a pre-defined flow rate. The flow rate is arrived from the quantity of effluent to be treated and providing a hydraulic retention time (HRT) of 3 d. The effluent from the stage I unit flows into stage II at a predetermined flow rate. The TSB process functions as follows. Biooxidation - Stage I: The organic pollutants in the equalized effluent are biooxidised by heterotrophic bacterial strains like *Pseudomonas, Bacillus, Paracoccus*, etc developed in the system depending upon the type of pollutants present in the process effluents. Most of the readily biodegradable organics including VOCs and phenols are removed in this stage. Biooxidation - Stage II: The autotrophic nitrifying bacteria (*Nitrosomonas, Nitrobracter, Nitrosococcus, Nitroribrio, Nitrospira sp.* etc) are developed for oxidizing ammonia present in the effluent from stage I in addition to biodegration of residual organics. The TSB process is a biological wastewater treatment process, having flexibility to treat any quantity of effluent generated at the industrial site. The TSB process can be adopted to establish a new treatment facility or can also be implemented to reengineer an existing treatment facility for delivering improved performance. The TSB process can help to improve the wastewater treatment.

Effectiveness and efficiency of the TSB process

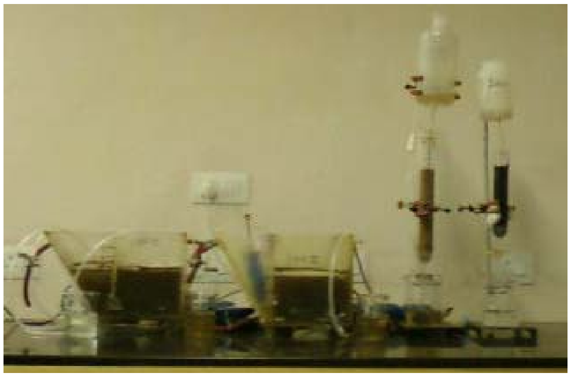
The TSB process is developed after optimization of operational parameters on laboratory scale using live wastewater and after successful trial runs at industry site. Since, the active consortia in the TSB process is developed from the microflora present in the existing biological facility, the process is robust and can effectively remove the pollutants from the effluent under consideration. The TSB process helps to generate effluent of the following characteristics, if operated under the design conditions, pH: 5.5-7.0; Ammonia ≤ 50 mg NH_4^+-N/L; COD≤ 250 mg/L; BOD ≤ 30 mg/L; Phenol ≤ 5 mg/L and Cyanide ≤ 0.2 mg/L. Depending upon the level of treatment efficiency needed to meet the end use requirement, the TSB process can be suitably combined with a downstream polishing step. The TSB process works in tandem as an individual treatment unit along with other treatment processes in an effluent treatment facility.

Salient features of the TSB process

- ✓ No chemical treatment involved
- ✓ Removal of both organics and ammonia including phenol and cyanide through biooxidation process
- ✓ Inhibition of nitrification in presence of organics is eliminated
- ✓ Two-stage separation process targets removal of specific pollutants in each stage through development of specific bacterial strains
- ✓ The microbial consortia are developed from the existing microflora, thereby reducing the adaptation period and increasing tolerance towards the pollutants in the wastewater

- ✓ Effective treatment achievable through adoption of sequential batch process operation for process effluents generated with wide fluctuation in flow and characteristics
- ✓ Highly flexible and the process can be tuned to the requirement of effluent treatment required
- ✓ The TSB process can be suitably ‘pre-fixed’ or ‘suffixed’ with other unit operations and/or processes present in an existing treatment facility thereby catering to site specific requirements
- ✓ Treated effluent conforms the desired effluent quality.

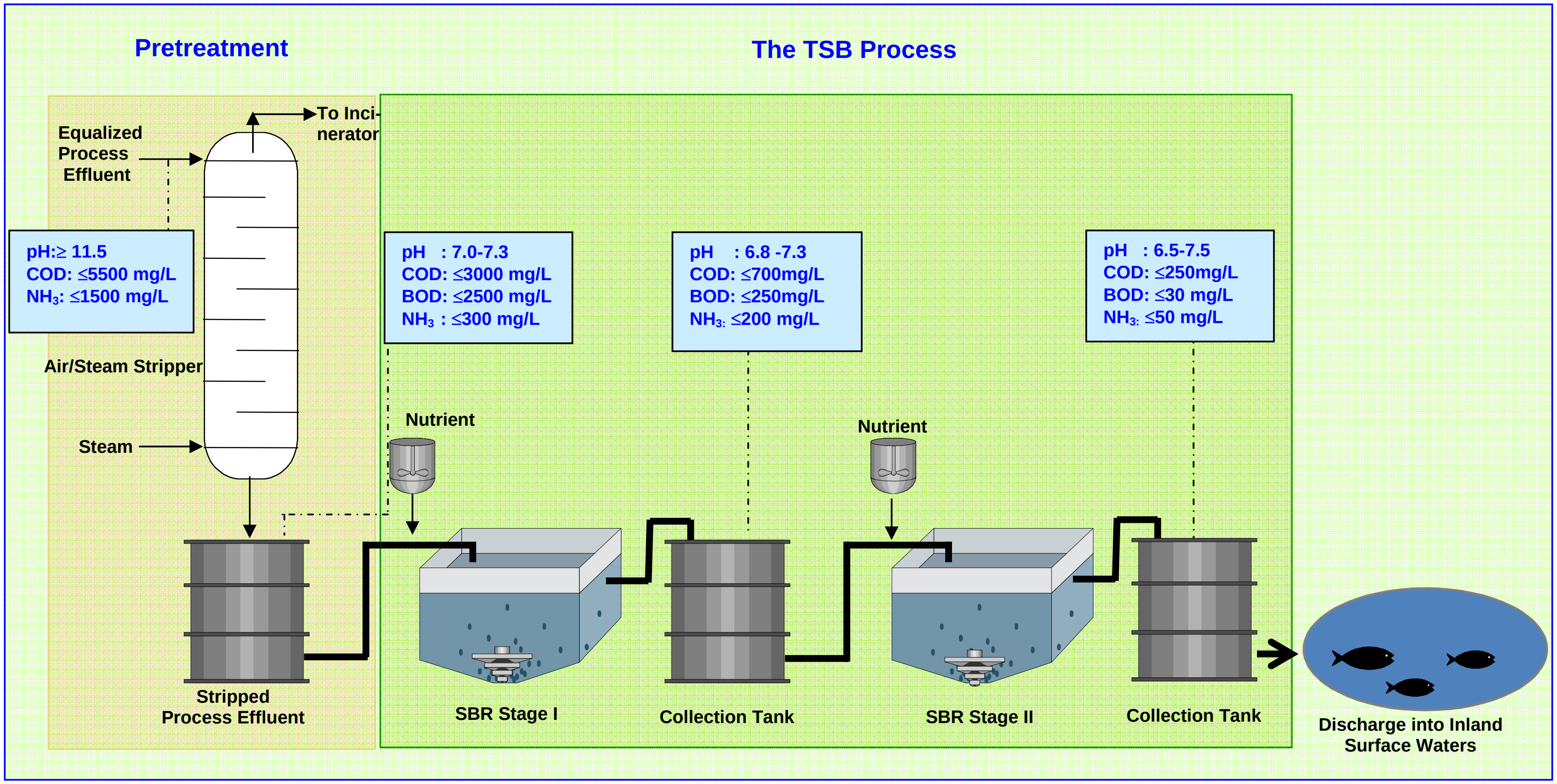
The TSB process has been successfully demonstrated on bench scale in an agrochemical industry



A

B

An experimental set-up of the TSB process (A) and its demonstration at an agrochemical industry (B)

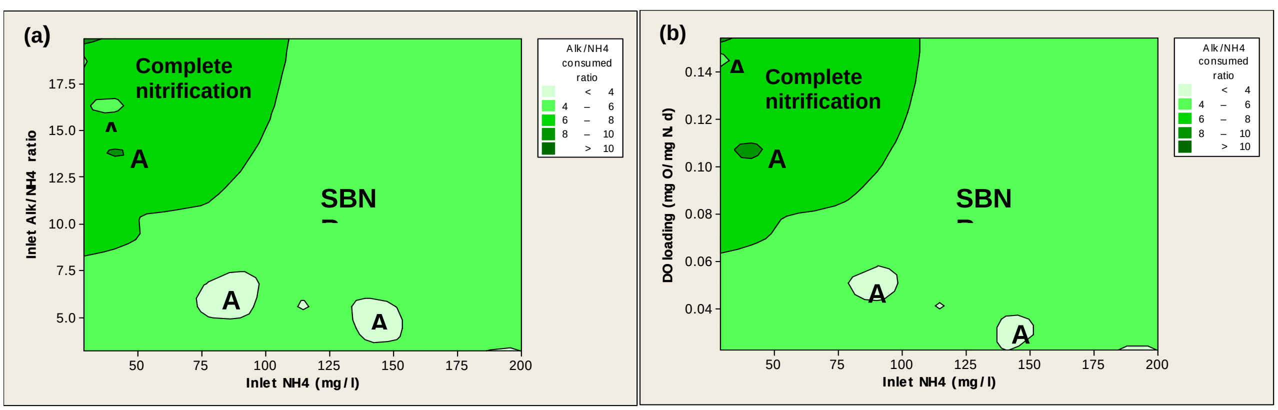


A schematic diagram of the TSB process

- **Single-stage biological nitrogen removal (SBNR) process for treatment of ammonia rich wastewaters**

Biological nitrogen removal (BNR) in wastewater treatment is mostly carried out by multi-step microbial processes. Because of high operation and maintenance cost, technologists at international level are now looking for 'single-sludge single-reactor' (SSSR) systems that preferably have low or nil oxygen requirement. Principally, the compact reactor configuration in single stage process such as OLAND process and CANON process is cost effective due to lesser oxygen demand, but technically, operational control is more sensitive than two-stage reactor process. Intricate control of process parameters is required to maintain balance between aerobic [ammonium oxidizing bacteria, (AOB) and nitrite oxidizing bacteria, (NOB)] and anaerobic (ANAMMOX) groups of ammonia oxidizers. To achieve nitrogen removal in a single stage biological process, the activity of NOB has to be inhibited without affecting the activities of AOB and ANAMMOX. In single stage processes developed internationally, nitritation is limited through imposing a DO and nitrite limiting condition, which is not sufficient. Hence, in a long run, such single stage processes have failed due to unwanted nitrate formation. By controlling bicarbonate alkalinity, the process of elimination of NOB can be further fine-tuned. The inclusion of alkalinity as a controlling parameter for achieving nitrogen removal in a single stage biological process is investigated by NEERI.

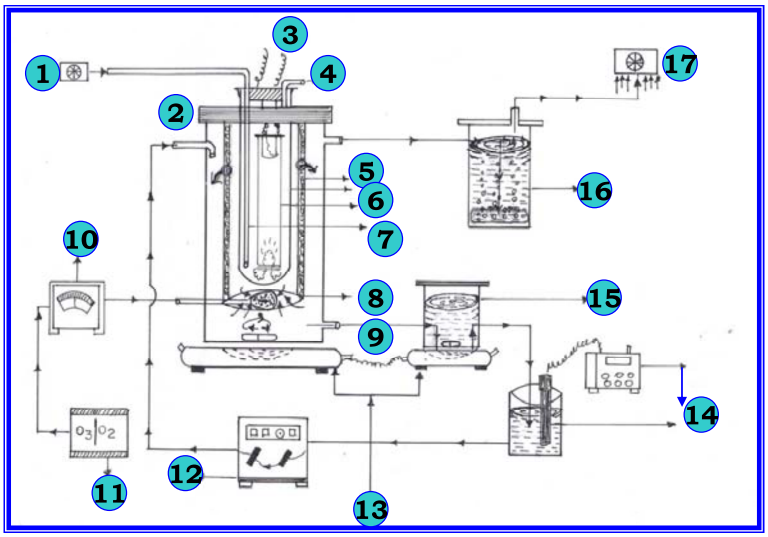
A SBNR process has been developed by NEERI using a laboratory scale fixed film bioreactor for anaerobic oxidation of ammonia to nitrogen. The process is based on a novel combination of partial nitritation and ANAMMOX process in a single stage. The oxidation of ammonia to nitrogen is achieved through a 'two-way' process control of alkalinity and dissolved oxygen (DO). The control of alkalinity and DO concentrations in feed is necessary for inhibiting of nitrification and for enhancing partial nitritation and ANAMMOX as can be seen from the contour plots in the figure. The fixed film bioreactor provides an ecological advantage for natural development of various microbial niches in a biofilm system and achieves stable autotrophic nitrification. The metagenome of the biofilm reveals presence of many hitherto unreported autotrophic microorganisms. The process is completely autotrophic and oxidizes ammonia with an efficiency of >85% at optimized conditions. The SBNR process is useful for treatment of ammonia rich wastewaters having very low C:N ratio. The SBNR process provides a future core area of anaerobic nutrient removal in wastewater treatment. The process has potential to emerge as a cost effective technology.



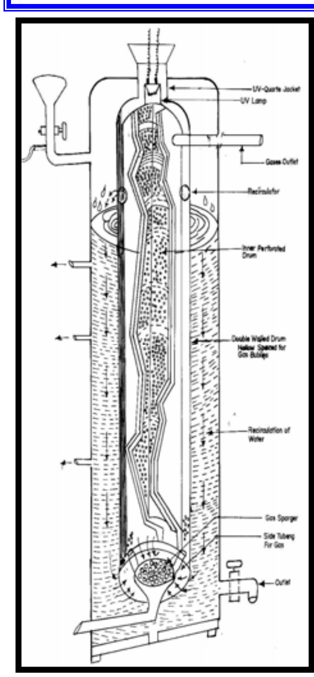
Two-dimensional contour plots of the two factor interaction models for consumed alkalinity to ammonia ratio: (a) showing effect of inlet alkalinity to ammonia ratio and influent ammonia and (b) showing effect of DO loading and influent ammonia. The deep green coloured zone indicates conditions favouring complete nitrification which is not desirable, while light green colour indicates conditions favouring partial nitritation that is desirable for SBNR process. Patches marked by 'A' are the periods wherein the reactor performance varied due to anomalous factors

- **Destruction of cyanide and pesticides through application of AOPs**

Advanced oxidation process (AOP) plays a crucial role in wastewater purification. AOP photo reactor was designed and fabricated with the help of easily available indigenous materials. The efficiency and reproducibility of the process and the reactor were evaluated by applying various combinations of AOPs for the treatment of cyanide and pesticides. The optimization of DWS AOP photoreactor was accomplished by three major steps: optimization process of individual AOPs, i.e. H_2O_2, O_3, TiO_2 and UV; optimization process of binary combination of AOPs, i.e. H_2O_2 + UV, O_3 + UV, TiO_2 + UV, H_2O_2 + O_3, H_2O_2 + TiO_2, O_3+TiO_2 and optimization process of tertiary combination of AOPs, i.e. H_2O_2 + O_3 + UV, H_2O_2 + TiO_2 + UV, O_3 + TiO_2 + UV, H_2O_2 + O_3 + TiO_2, H_2O_2 + O_3 + TiO_2 + UV. Among all individual AOPs, application of H_2O_2 was found to be the best process for the destruction of cyanide and pesticides from 10 ppm to 0.02 ppb. In binary process, a combination of H_2O_2 + UV was found to be the best for the destruction of both cyanide and pesticides from 10 ppm to 0.02 ppb. In tertiary process, a combination of H_2O_2 + O_3 + UV was the best amongst other combinations considering economy, doses of AOPs, time and specific energy consumption.



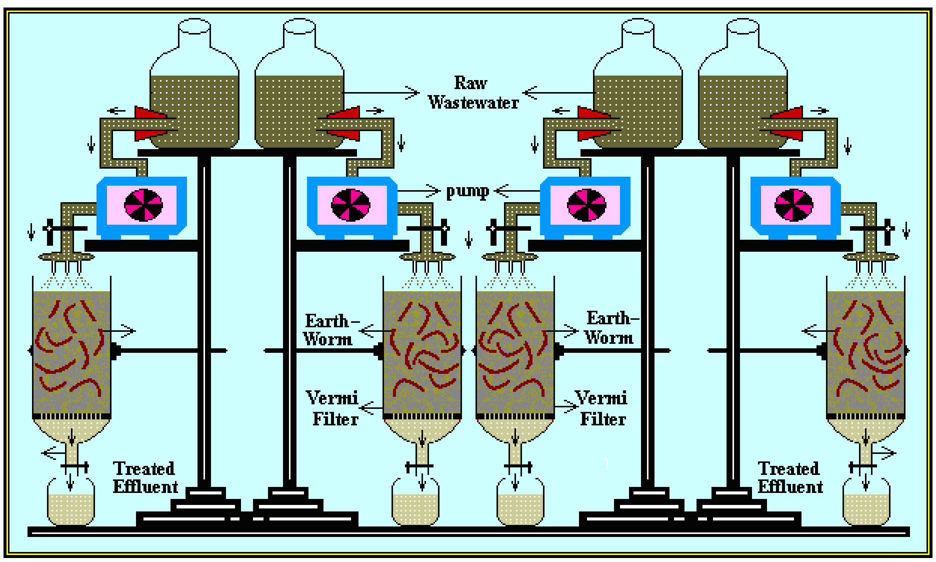
1. Cool Air
2. Inlet
3. Electrical Connections
4. Hot Air Outlet
5. Doubled Walled Sieved Cylinder
6. UV Lamp / Quartz Jacket
7. Air Cooling Tube
8. Ozone Diffuser
9. Outlet of Wastewater
10. Ozone Meter
11. Ozone Generator
12. Peristaltic Pump
13. Magnetic stirrer
14. pH & Ion Meter / Electrode
15. External Mixing Chamber
16. CN & Flue Gases Scrubber
17. Final Exhaust



Experimental set-up of AOP photoreactor

- **Vermifilters: A tool for aerobic biological treatment of herbal pharmaceutical wastewater**

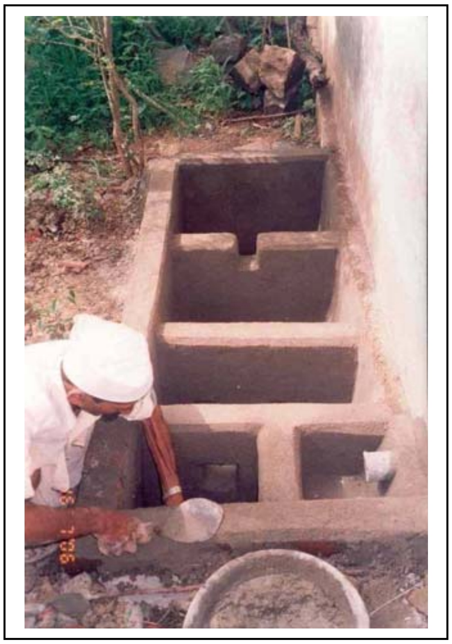
Herbal pharmaceutical wastewater possesses high chemical oxygen demand (COD) (21,960–26,000 mg/L), biochemical oxygen demand (BOD) (11,200–15,660 mg/L) and suspended solids (SS) (5,460–7,370 mg/L). It cannot be directly discharged into surface water bodies, due to its highly biodegradable nature. Herbal pharmaceutical wastewater has been treated by using vermifilter, which is an ecosystem consisting of biosoil with bacteria and earthworms producing vermicastings. In the present studies, a cost-effective, eco-friendly and sustainable method has been applied for the treatment of herbal pharmaceutical wastewater using earthworms. Studies were carried out at different organic loadings, ranging between 0.8 and 3.2 kg COD/m^3 day at three different hydraulic loadings of 1, 2 and 4 days. Vermifilters packed with 1:1:1 ratio of soil, sand and vermicast as media matrix along with the twenty adult earthworms in each reactor were used for the experiments. Treated effluent was colour and odour free. Efficient COD/BOD removals in the range of 85.44%–94.48% and 89.77%–96.26% were obtained respectively at 2 days hydraulic retention time (HRT). Heavy metal removals were also observed and no sludge production problem was encountered, only nutrient rich vermicast from the filters was removed and analyzed after the experiments. It showed higher manurial value than control in terms of available nitrogen, phosphorus and potassium (NPK) and were found in the range of 178.75–278.75 kg/hectare of available nitrogen, 16.128–50.4 kg/hectare of available phosphorus and 19.3–28.6 kg/hectare of available potassium at maximum HRT and at different organic loadings. The feasibility of vermifilters in herbal pharmaceutical wastewater treatment at different organic and hydraulic loadings was studied in detail.
(The paper published in Water Science & Technology- WST, 61.9, 2375-2380, 2010; Authors: Dhadse Sharda, Satyanarayan Shanta, Chaudhari P R and Wate S R)



A schematic diagram of aerobic biological treatment of herbal pharmaceutical wastewater

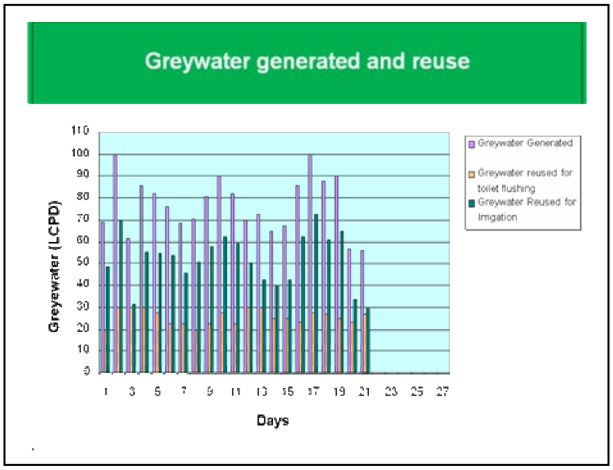
- **Grey water treatment and reuse**

NEERI was involved in development of grey water treatment and reuse systems at institutional and household levels. The grey water reuse systems collect, treat and reuse bathroom water (shower, non-toilet/ black water) for flushing of toilets. The drive for this technology was a result of decreasing availability of water and lowering of groundwater table. Grey water treatment plants constructed in the institutions, particularly in residential schools (Ashrams) in Madhya Pradesh, mainly consist of sedimentation or settling unit and filters. Process of sedimentation allows removal of suspended solids by gravity and natural aggregation of the particles without use of coagulants. The major processes in filtration are sedimentation in the pore spaces, adhesion to the media particles, and bio-chemical degradation of captured particles in slow-sand filter. The concept of grey water reuse from the institutions has been extended to the households to treat and recycle grey water. This system also consists of sedimentation and filtration, and possible reuse of treated grey water includes toilet flushing and irrigation. A design of grey water treatment system developed at household level is shown below.



In order to conserve water by recycling and reuse of grey water as an alternative source for toilet flushing and gardening / irrigation etc, a NEERI residential quarter was selected to study the detailed quantification, characterization and reuse of wastewater generated from bath, wash basin and laundry (excluding kitchen wastewater). Grey water treatment plant was designed and constructed for a flow of 480 lit/day as shown below.

Based on the daily observations, daily potable water demands for a household and grey water generation from bath, laundry and wash basins were observed to be 165 LPCD and 80 LPCD respectively. And for reuse for toilet flushing and irrigation of an area of 22 sq m the water demands calculated to be 24.50 LPCD and 46 LPCD respectively. The following diagram shows the grey water generation and reuse on per capita basis for a period of three weeks.



The study revealed that about 40% to 60% potable water can be saved by reuse of grey water. It is estimated that about Rs. 6 lakh / year water charges can be saved if recycled grey water is used for gardening, irrigation and for toilet flushing in the households of NEERI Colony. Recycling and conservation of water in urban areas is therefore an essential contribution to the future environmental sustainability. The performance of grey water treatment plant based on the grey water quality was assessed. It is found that the BOD and COD were removed on an average 82% and 61 % respectively.

Grey water for toilet flushing

Grey water for irrigation

• **Digital arsenic field kit**

A portable and innovative arsenic field kit with digital display for on-site screening of water sources for contamination of arsenic has been designed and developed by NEERI. The kit is battery operated and can be easily used for field measurement of arsenic. The kit has been subjected to laboratory and field evaluation and is found to be very precise and accurate. It is very sensitive in the range of 10 ppb to 100 ppb, 10 ppb being the WHO standard permissible value for arsenic in drinking water.

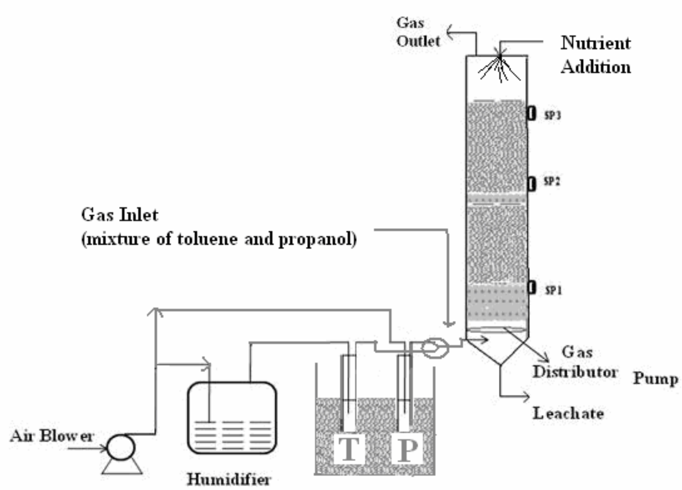
• **Aerobic biodegradation pathway for Remazol Orange by *Pseudomonas aeruginosa***

Removal of azo dyes from effluent generated by textile industries is rather difficult. Azo dyes represent a major class of synthetic colorants that are mutagenic and carcinogenic. *Pseudomonas aeruginosa* grew well in the presence of Remazol Orange (RO) and was able to decolorize and degrade it. In the present study carried out by NEERI, the decolorization and degradation efficiency using single culture *P. aeruginosa* with RO and textile wastewaters is studied. The elucidation of decolorization pathway for *P. aeruginosa* is of special interest. The degradation pathway and the metabolic products formed during the degradation were also predicted with the help of high performance liquid chromatography, Fourier transform infrared spectroscopy, and nuclear magnetic resonance spectroscopy analysis. The data show the cleavage of the azo dye RO to form both methyl metanilic acid and 4- aminobenzoic acid after decolorization and finally to oxidation forms benzoic acid, alkenes, aldehydes, and alkynes. The organism was able to decolorize the dye RO and wastewater effectively to the maximum of 82.4% and 62%, respectively.

[The paper has been published by K. Sarayu and S. Sandhya in *Appl Biochem Biotechnol* ,160:1241–1253 (2010)]

• **Development of a novel immobilized bioreactor for the treatment of mixture of VOCs at higher concentration with reference to volatility and water solubility**

The R&D activities related to development of a novel immobilized bioreactor system for the treatment of mixture of VOCs, viz. toluene and propanol, at higher concentration with reference to volatility and water solubility have been carried out using biofilter packed with compost and woodchips. The process parameter required for the scale up has been generated experimentally and the finding has been analyzed using a mathematical model. The most of the results cited in the international literature are based on a single VOC, either toluene or propanol, however, in this study carried out by NEERI, two VOCs in a mixture have been evaluated at a time using a novel immobilized bioreactor.



A schematic diagram of the bench scale biofilter treating toluene and propanol

Bench scale bioreactor treating toluene and propanol