

Bose & Bhattacharjee, 2015

Volume 1 Issue 2, pp. 15-29

Year of Publication: 2015

DOI- <http://dx.doi.org/10.20319/mijst.2015.12.1529>

This paper can be cited as: Bose, A., & Bhattacharjee, K., (2015). Bio-Algal Gas Cleaning Plant for Treatment of Blast Furnace Wastewater. MATTER: International Journal of Science and Technology, 1(2), 15-29.

This work is licensed under the Creative Commons Attribution-Non Commercial 4.0 International License. To view a copy of this license, visit <http://creativecommons.org/licenses/by-nc/4.0/> or send a letter to Creative Commons, PO Box 1866, Mountain View, CA 94042, USA.

BIO-ALGAL GAS CLEANING PLANT FOR TREATMENT OF BLAST FURNACE WASTEWATER

Abhishek Bose

*Indian Institute of Technology,
Kharagpur, West Bengal, India
boseabhishek95@gmail.com*

Korok Bhattacharjee

Indian Institute of Technology, Kharagpur, West Bengal, India

Abstract

The perennial problem is of treating harmful effluents from metallurgical processes is an interesting field of environmental innovation. A number of metallurgical industries utilize a lot of water for processes such as leaching, floatation, extraction and washing purposes. These wastewater effluents are different from other wastes as they contain salts of heavy metals, complex compounds and cyanides which have been found to be very harmful to the environment. Blast furnaces primarily use water to wash down waste materials from the ore after processing. This wastewater mainly contains dissolved salts, suspended solids, cyanides, chlorides, ammonia and trace amounts of other contaminants. A novel pathway for treatment of this blast furnace wash water is being suggested which utilizes microbial action on these compounds to break them down into harmless compounds which can be easily removed from the effluent stream. Cyanides and ammonia are the major pollutant which is being treated with microbial activity. The proposed pathway also allows harvesting biomass which can be used for the auxiliary production

of biofuels from wastewater treatment.

Keywords

Wastewater Treatment, Blast Furnace, Microbial Action, Biomass, Biofuels

1. Introduction

The road ahead is to determine a cost effective and innovative solution for the treatment of cyanide and chloride wastes in the effluent stream. With the advances of biotechnology and versatility of engineering, it can be proposed to design a reactor which utilizes microbial action to degrade cyanides into less harmful nitrogenous compounds. The removal of chloride and other salts should also be taken into account as they corrode the pipelines, increasing maintenance costs.

2. Operating Conditions

The input effluent stream is considered to have a high concentration of dissolved solids and other compounds washed down from the blast furnace. Modern blast furnace operations allow minimal use and wastage of water resources.

An approximate calculation led to the estimate of about 0.1 m³ of water being required for every metric ton of crude steel generated. From the production data in past years the total water requirement per day was calculated to be around 280 m³/day (Sharma, et al., 1977).

Table 1: Operating Conditions

COMPONENT	INPUT	OUTPUT
TSS	900 mg/L	Negligible
TDS	700 mg/L	Low
Chlorides	500-1000 mg/L	Low
Cyanides	2-8 mg/L	Less than 1 mg/L
pH of Input In Input I Stream	8-9	7
Temperature	40-50°C	

Cooling Tower

Cooling Towers are used to cool down the hot water from a temperature range of 45- 40^o C to around 30^o C (which is optimum temperature for algal growth) by bringing the warm water and air for evaporative cooling. Induced draft cooling towers are preferably used here with a counter-flow scheme.

The cooling tower is a necessity in the process considering the optimum temperatures for algal bloom in the bioreactor is around 30^oC where optimum enzyme activity is observed

Table 2: Design Specifications of Cooling Tower

Cooling Tower Design	
Height of Cooling Tower	2 m
Effluent Flow Rate	11.67 m ³ /hr
Inlet water Temperature	40 ^o C
Outlet water Temperature	30 ^o C
Dry Bulb Temperature of Air	31 ^o C

Nutshell Filter

The proposed primary treatment method requires the removal of suspended solids in the medium for higher purity and sludge removal which might result in clogging of the pipes and higher fouling.

The Nut Shell (Godos, et al., 2011) uses adsorption technology for oil coalescing. It includes a filter bed that adsorbs the TSS which is recharged during backwashing. The water is pumped through the bed which takes up the TSS as the water percolates through its pores. The bed is kept within an optimum density range. This enables the bed to filter the water to the required purity at the desired rate. The nutshells, which generally c o m p r i s e of pecan and walnut shells, have excellent surface characteristics for coalescence, filtration, and high “modulus of elasticity”, (Exterran).

Table 3: Specifications of Nutshell Filtration Unit

NUT SHELL FILTRATION UNIT	
Total effluent load	280 m ³ /day
Packing density	0.8 g/cc
Approximate Area	0.353 m ²
Volume	0.494 m ³
Recurring cost estimate	Rs 356 / year
Cost of electricity	Rs 521 /day
Recharge Time	20-30 minutes/ 24 hours
Height of packing	1.676 m
Input TSS	900 ppm

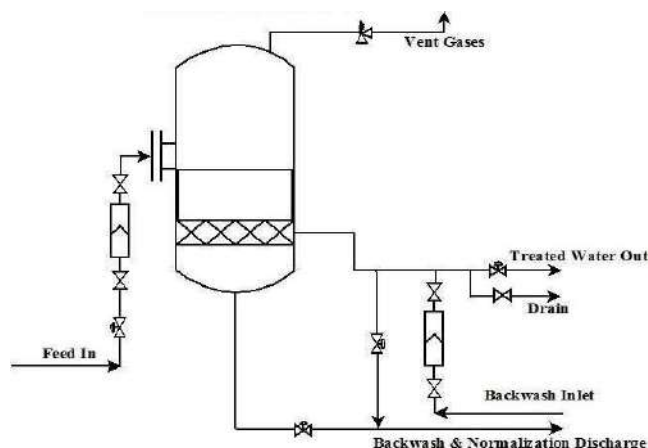


Figure 2: Nut Shell Filtration Unit

Some Common Mistakes

The removal of TSS has to be subsequently followed by the removal of the dissolved solids in the effluent medium including chlorides, metal salts, and sulphates and dissolved impurities. This can be brought about by a reverse electro-dialysis setup. An electro-dialyser is an electrochemical separation process in which ions are transferred through ion exchange membranes by means of a direct current (DC) voltage. (Veerman, 2010). The process uses a driving force to transfer ionic species from the source water through cathode (positively charged ions) and anode (negatively charged ions) to a concentrated wastewater stream, creating a more

dilute stream. ED selectively removes dissolved solids, based on their electrical charge, by transferring the brackish water ions through a semi permeable ion exchange membrane charged with an electrical potential. EDR works the same way as ED, except that the polarity of the DC power is reversed two to four times per hour. This polarity reversal helps prevent the formation of scale on the membranes. (Figure 4)

Storage Unit Mechanical Design

The concentrate stream of the electro-dialyzer needs to be continuously diluted and re-fed into the system during the operation. This storage unit acts as a balancing tank which stabilizes the physical parameters of the concentrate stream of electro-dialyzer, (Reversed electro dialysis).

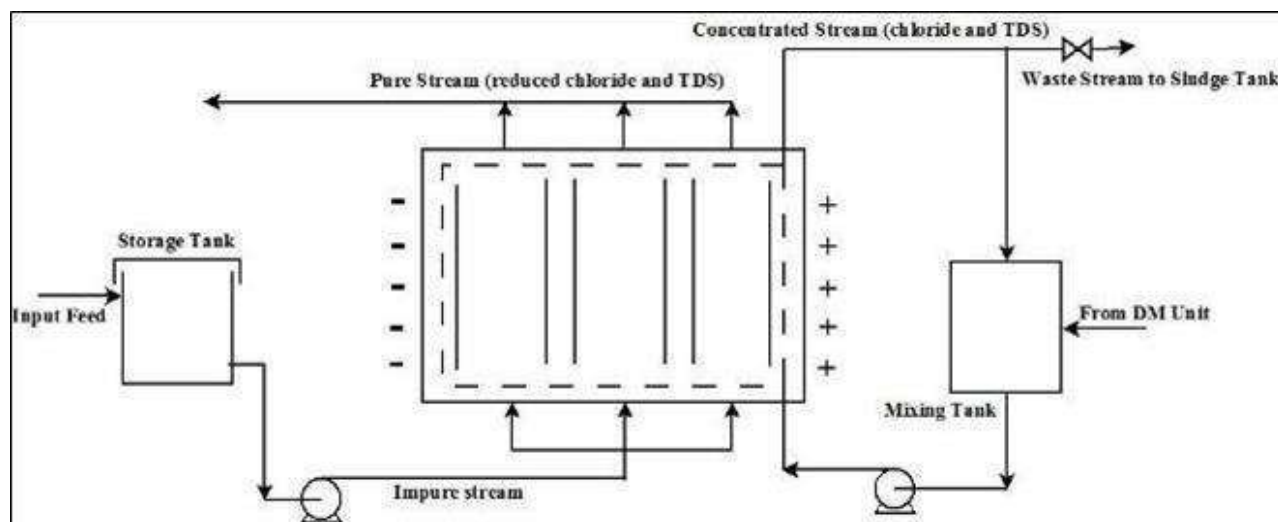


Figure 3: Design of a Reverse-electro dialysis system

5. Cyanide Removal from Wastewater

The main goal of the proposed waste water treatment plant is the detoxification of Cyanide containing compounds in the wastewater used in the Blast Furnace. A proposal is being proposed for a photo-bioreactor which uses Algal photosynthesis to degrade cyanide compounds into less toxic products (Scenedesmus).

A photo-bioreactor is a newly developed technique for required industrial algal production or for cultures of other microorganisms. The reactor uses cultures of Scenedesmus obliquus, a blue green algae of the genus Cyanophyceae to convert Cyanide into nitrogenous compounds.

The reactions are catalyzed by photosynthetic enzymes and can be assumed to follow

Michaelis-Menten Kinetics, (homealgaeproject).

Design of Photo-Bioreactor

Initial algal cultures are produced on a small scale by introducing nutrient rich compounds into the substrate after obtaining a pure strain of the required species. The cultures are then fed into a fed batch, air agitated photo bio-reactor. The wastewater to be treated is introduced in batches of 2-3 hours depending on the exact calculated residence time requirement for the detoxification.

The main feature of a bio-reactor is to allow a higher surface area to volume ratio for the reactor so as to be able to increase the penetration of light in the bulk of the system for efficient photosynthesis. A novel design is being proposed which consists of an array of smaller tubes being present inside a larger tank. The void spaces in between are to be fitted with LED or fluorescent light sources for efficient distribution of luminous flux, (Industrial-Size-Photo-Bio-Reactors).

The required intensity is of the order of 400 lux which can be easily provided by fluorescent lamps along with sunlight penetrating into the glass tubes. Light intensity should be controlled so as to prevent photo-bleaching of the algal cells. The carbon dioxide requirement for photosynthesis can be easily met by air sparing of the reactor and hence, a separate CO₂ gassing system need not be designed for the proposed setup. The population density of the algal culture is initially considered to be around 9×10^6 cells/ml of solution which rises to almost double the amount after the growth of algae by detoxification. The end products of cyanide degradation are ammonium salts and trace organic matter which are considerably less toxic (Wagner, et al., 1996).

Table 4: Design Characteristics of Photobioreactor

Detail Design Characteristics			
Residence Time required(approx)	3 hours	Optimum CO ₂ concentration	1500 ppm (max)
Volume to be treated in one batch	35	Algal Species	<i>Scenedesmus obliquus</i>
Number of parallel reactors used	6	Wastewater to be treated	280 m ³ /day
Number of tubes in the reactor	24	Ammonia Concentration	9-10 mg/L

Diameter of tubes	0.325 m	Input Cyanide Concentration (CNi)	2-8 mg/L
Height of Reactor cylinder	3 m	Ammonia Concentration	9-10 mg/L
Material of Construction	Perspex Glass	Output Cyanide Concentration	<1 mg/L

An air sparger is used for supplying the necessary carbon dioxide required by the algal biomass. The produced oxygen and excess air is exhaled from the reactor through a breather valve to maintain pressure in the tank. It has been observed that bioreactors have kinetics which are generally inhibited by the micro mixing in the reaction vessel. Mixing is induced by bubbling air in the tubes, which have a considerably lower diameter thereby encouraging higher Reynolds number flows and a better mixing coefficient. Void spaces in the reactor are fitted with fluorescent lamps to increase the intensity of the light for photosynthesis. The productivity of the reactor is accentuated by the presence of ammonia and nitrogenous components in the feed stream which act as nutrient medium.

Oxidative Reactions:- $\text{HCN} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{NH}_3$ - $\text{CH}_2=\text{NH} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CH}_4 + \text{NH}_3$ (1)

Reductive Reactions:- Cyanide monooxygenase $\text{HCN} + \text{O}_2 + \text{H}^+ + \text{NAD(P)H} \rightarrow \text{HO-CN} + \text{NAD(P)}^+ + \text{H}_2\text{O}$ (2)

Cynaide dioxygenase $\text{HCN} + \text{O}_2 + 2\text{H}^+ + \text{NAD(P)H} \rightarrow \text{CO}_2 + \text{NH}_3 + \text{NAD(P)}^+$ (3)

Reasons for Selection of Scenedesmus Obliquus

Scenedesmus Obliquus is a species of algae of the class Chlorophyceae (MBBR). These are freshwater algae, easily growing having higher growth rates. This is selected particularly for its high cyanide fixing ability in a wide range of concentrations. The expected time for degrading 100 mg/L of cyanide containing wastewater was found to be around 24 hours. The available experimental data can be extrapolated at lower concentrations to find the residence time needed in the bioreactors. It is estimated that 35-40 % of the cyanide breakdown takes place in the first hour of agitation. (Industrial-Size-Photo-Bio-Reactors) Data for Chlorella sp and other alga are also available.

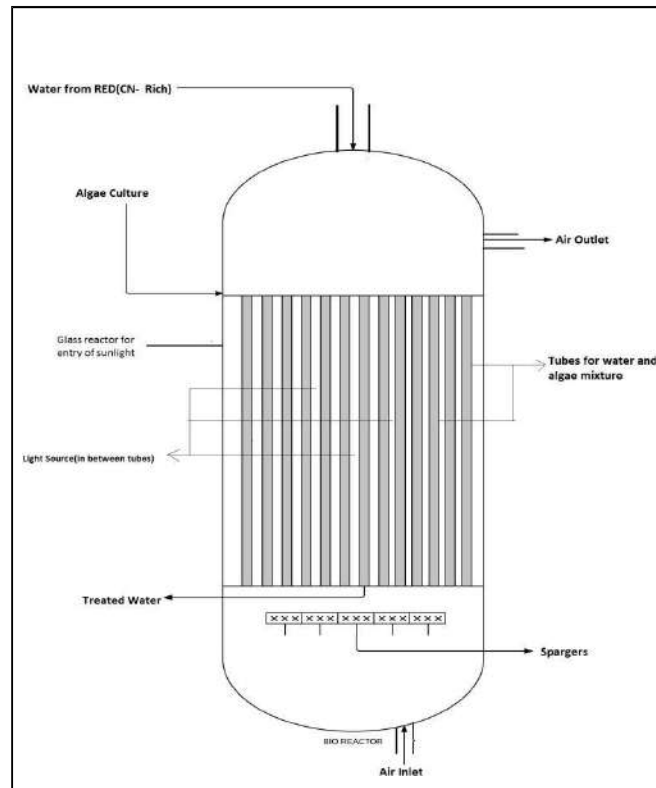


Figure 4: Schematic Diagram of Photobioreactor

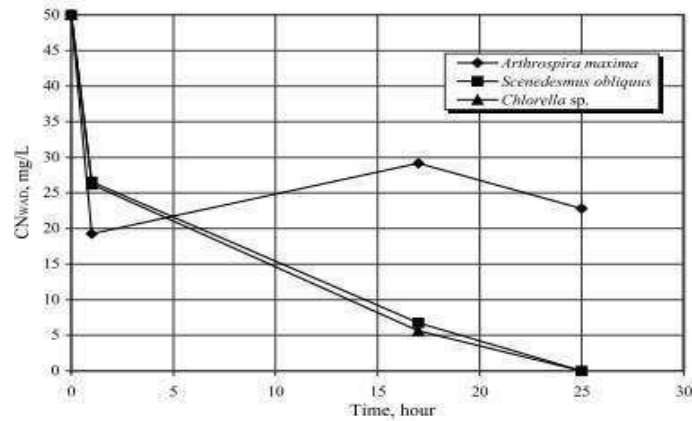


Figure 5: Comparison of reaction rates of different algal strains

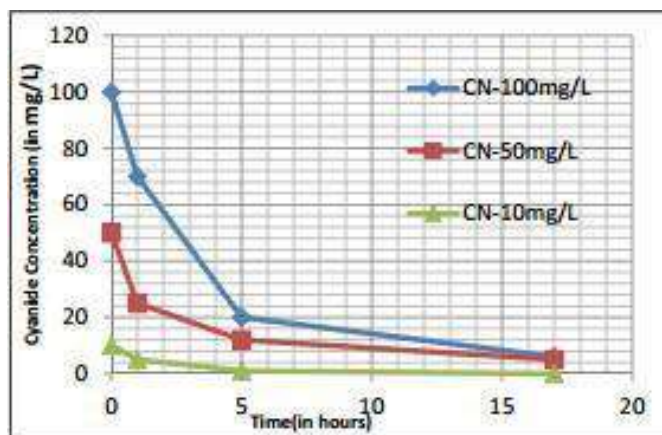


Figure 6: Comparison of rates for varying cyanide concentrations

Algal Culture Tank

A pure strain of *S. Obliquus* is obtained by laboratory cultures and then scaled up in a culture tank. The tank serves as a primary growth of algal biomass and is inoculated with a nutrient medium. The medium was essentially composed of KNO_3 0.1 g; $\text{K}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ 0.02 g; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 0.001 g; $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 0.001 g and 50 ml of soil extract for a liter. The algal biomass is then transferred to the bioreactor where the effluent degradation takes place.

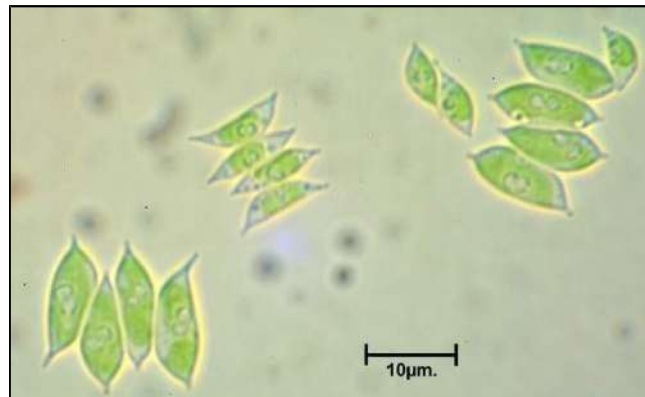


Figure 7: Optical Microscope images of *Scenedesmus sp.*

6. Efficient Removal of Biomass from Wastewater

Biomass removal can be a cumbersome process if not dealt properly. Uncontrolled growth and algal bloom is harmful for the system in question as it results in unwanted compounds being released into the system. The most effective method for the removal of algal biomass from the wastewater stream would be by the addition of flocculating agents which

effectively clump the biomass and allow precipitation and removal of biomass. (MBBR) Flocculating agents of many kinds are used but maximum efficiency is obtained for Polyacrylamide (PAM) based additives which show high flocculating action at low concentrations of 5mg/L. (Holzbecher, 2012). The flocculation can be hastened by the sparing of air which initiates greater contact and mixing followed by settling. The clumped biomass can be separated from the treated wastewater by mechanical screening methods or precipitation of the clumped biomass.

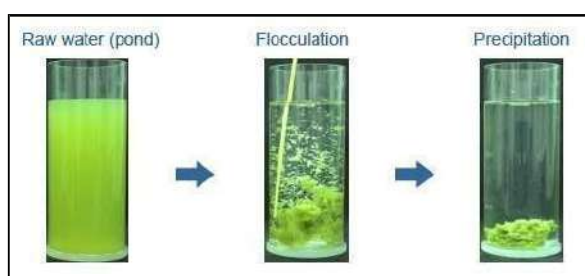


Figure 8: *Flocculation and removal of algal biomass from treated wastewater*

Post-Treatment of Collected Biomass and Conversion in Biofuels

The collected biomass can be collected from the flocculation tank and sent for production of Biofuels in order to harness the energy rich algal source.

Conventional techniques which have already been industrially viable include the separation of lipids from the other components of the biomass (Gurbuz, et al., 2004). This however leads to a loss in biomass amount and low yield in combustible fuel. In general a solvent extraction process is carried out which uses a commonly used solvent such as n-hexane to dissolve and separate the lipid component in the biomass followed by conversion to Biodiesel. (Mc-hill, 2008).

A secondary method has been recently established and promises greater yield of biofuels can be used instead as well. This method as developed by the Pacific Northwest National Laboratory. (Process Group Ltd), promises higher yield by utilizing the entire biomass slurry for the production. By utilizing hydrothermal treatment procedure it makes use of the entire amount of biomass, resulting in the production of Biodiesel, fuel gas, nutrients such as P, K, etc which are recycled back along with excess water which is again fed back to the stream. The process of biofuel production is still in the primary stage and pilot plant scale ups are in order to

determine the feasibility of the processes involved.

7. Removal of Ammonia and Ammonium Ions in the Wastewater Stream

Ammonia is an essential nitrogen source for the algal growth in the bio-reactor for cyanide degradation. The cyanide salts are broken down into ammonium salts in the solution which consequently increases the ammonia content in the solution. Ammonia dissolved in solution in the form of ammonium ions, which can be removed easily by the process of nitrification by several species of bacteria (Process Group Ltd).

The design of a nitrification tank is being proposed which utilises *Nitrosomonas* sp and *Nitrobacter* sp (Pacific National Northwest Laboratory) in a Moving Bed Biofilm Reactor (MBBR). (World Bank Guideline) Industrially scalable models are already available which provide a large surface area of contact, better settling and less sludge production. Also, it can be fitted with existing apparatus which are being used to handle the wastewater, thereby reducing costs. The bacterial cultures can be easily obtained from soil and a packed bed of substrate can be used to pass the wastewater through the system.

The nitrified wastewater is then passed into a denitrifying system which used the MBBR scheme and helps in converting the inorganic nitrate residues from nitrification into nitrogen gas which can be liberated into the atmosphere producing minimal sludge. Bacterial species of *Pseudomonas* and *Paracoccus denitrificans* might be commonly used owing to their ease of availability and high activity. The final effluent water is stated to reach an almost negligible ammonia concentration thereby reducing possibilities of algal bloom and biomass degradation.

8. Final pH Treatment and Recycle of Wastewater

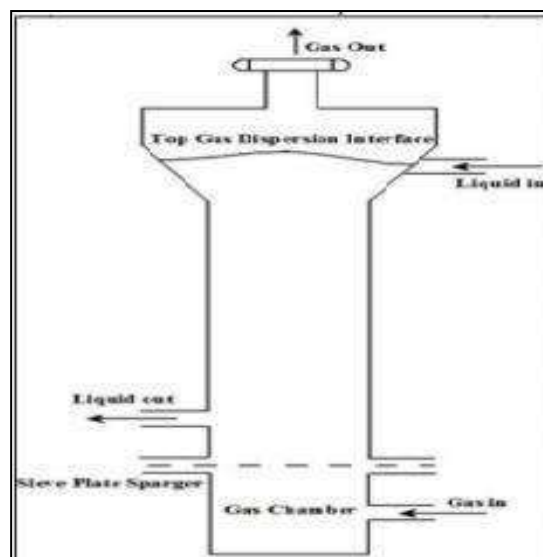
The effluent stream has an inherent alkaline nature which is essential for carrying out the purification processes. In order to maintain the final pH to a neutral level, the waste water is passed as a counter current to the flow of the flue gas from the plant itself. The density difference of the bubble of the flue gas formed in the cylindrical tank causes the bubble size to increase as it rises up the column. The flue gas (FG) is acidic and it neutralizes the alkalinity of the waste water (Code of Practice for small wastewater plants).

Table 5: pH Controller Design

design Specifications for pH Controller	
pH of input stream 9	9
Total volume of effluent to be treated	280 m ³ /day
Residence Time 10 mins	10 mins
Diameter	0.8 m
Height	2.4m
Flue Gas flow rate 14.14 L/ hr	14.14 L/ hr
Concentration of Sulphur	< 1 ppm (negligible)

Design of pH Controller

A cylindrical tank is fitted with a circular sieve plate. This plate is having circular holes that allow for the flow of flue gas. Gas is supplied to these spargers by a header which is expected to execute uniform supply to all the pipes. The flue gas mainly enters the gas chamber and its flow is determined by the distribution and number of holes on sieve plate. The acid gases are scrubbed by the effluent liquid to increase the acidity of the stream to a neutral level.



9. Conclusions

The proposed water treatment plant is expected to be an efficient, self-supporting process with minimal running and maintenance costs. The key features of the plant are the utilization of biological means to degrade the harmful compounds in the effluent stream. Photo-bioreactors have a great potential to be scaled up for industrial scale processes. The minimal energy requirements coupled with high biomass production rate makes it suitable for removal of cyanides and harmful compounds. In addition the proposed design uses eco-friendly materials such as nutshell filtration units, which have very less environmental hazard. Use of bacteria for removal of nitrogenous compounds results in the formation of organic and inorganic nitrates which can be added as nutrient additives for local fertilizer industries as well. Wherever possible, recycling and reuse of the existing products has been suggested such as pH treatment with flue gas from the plant, which reduces wastage and costs as well. The process however cannot be operated continuously but in batches as the products require higher residence time for complete bio-treatment.

10. Acknowledgement

This research was supported by the Department of Chemical Engineering, IIT Kharagpur. The authors would like to thank our friends, Professors and co-researchers who provided great help and suggestions in enabling us to present the conclusions from this study.

REFERENCES

- Sharma, B., & Ahlert, R. C. (1977). Nitrification and nitrogen removal. *Water Research*, 11(10), 897-925.
- Gurbuz, F., Ciftci, H., & Akcil, A. (2009). Biodegradation of cyanide containing effluents by *Scenedesmus obliquus*. *Journal of hazardous materials*, 162(1), 74-79.
- Naveen, D., Majumder, C. B., Mondal, P., & Shubha, D. (2011). Biological treatment of cyanide containing wastewater. *Res J Chem Sci*, 1(7), 15-21.
- De Godos, I., Guzman, H. O., Soto, R., García-Encina, P. A., Becares, E., Muñoz, R., & Vargas, V. A. (2011). Coagulation/flocculation-based removal of algal– bacterial biomass from piggery wastewater treatment. *Bioresource technology*, 102(2), 923-927.
- Deep Bed Nutshell filter evolution – Exterran. dissertations.ub.rug.nl/faculties/science/2010/j-

veerman.

en.wikipedia.org/wiki/Reversed_electrodialysis.en.wikipedia.org/wiki/Scenedesmus.

<http://www.et.byu.edu/~wanderto/homealgaeproject/Harvesting%20Algae.html>.

<https://www.scribd.com/doc/11570310/Industrial-Size-Photo-Bio-Reactors>.

Wagner, M., Rath, G., Koops, H. P., Flood, J., & Amann, R. (1996). In situ analysis of nitrifying bacteria in sewage treatment plants. *Water Science and Technology*, 34(1), 237-244.

MBBR for nitrification by Corey Bjornberg. MBBR for nitrification by Corey Bjornberg.

Holzbecher, E. (2012). *Environmental modeling: using MATLAB*. Springer Science & Business Media.

Gurbuz, F., Ciftci, H., Akcil, A., & Karahan, A. G. (2004). Microbial detoxification of cyanide solutions: a new biotechnological approach using algae. *Hydrometallurgy*, 72(1), 167-176.

Perry's chemical engineers' handbook. Vol. 796. New York: McGraw-hill, 2008. Process Group Ltd. - Nut Shell Filters.

The promise of microalgal-derived biofuels - Pacific National Northwest Laboratory. World Bank Group, Environment, Health and Safety Guidelines. www.epa.vic.gov.au - Code of Practice for small wastewater plants. www.oilgae.com/algae/oil/extract/che/che.html.