Anaerobic Treatment of Inhibitory Compounds of Agro Based Pulp & Paper Mill Effluents-Various Pretreatment Options

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ABSTRACT

Anaerobic treatment systems have been successfully applied over the last decades for treating pulp & paper mill effluents, mainly the recycled effluents. However, the anaerobic treatment of certain waste water streams is limited due to the presence of recalcitrant (toxicants/ inhibitory) compounds such as resin, chlorinated phenols & inorganic sulphur compounds in pulping & bleaching spent liquors which make these water toxic to microflora. But the recent developments in anaerobic reactor technology & various other techniques have opened the avenues for the commercial exploitation of anaerobic treatment systems for toxic waste water streams. In order to improve the biodegradability of these effluents various pretreatment options may be incorporated. The microflora can be adapted to the toxic/inhibitory compounds- the highly polluted waste water streams can be diluted with less polluted streams to decrease the concentration of recalcitrants below threshold limit, detoxification of waste water could be achieved by physico-chemical/ biological means and attached growth reactors which are generally less sensitive to toxicity can be employed for the treatment. A combination of anaerobic treatment is necessary for the successful operation of anaerobic treatment of toxic waste waters. The present paper discusses the various pretreatment options/measures which can be combined with anaerobic treatment to make pulp & paper effluents more amenable/ susceptible to the process in order to exploit its potential advantages with particular reference to small pulp & paper mills in the country - the major source of pollution in the pulp & paper sector.

INTRODUCTION

In recent years anaerobic processes have been increasingly & successfully applied as an alternative to the conventional aerobic treatment processes for the removal of organic pollutants from easily biodegradable & non-toxic waste waters of industrial origin. Most of the full scale installations have come up to treat easily biodegradable waste water streams in pulp & paper mills like TMP, paper mill effluents composed of easily degradable carbohydrate degradation products & evaporator condensates which are mostly composed of alcohols & volatile fatty acids. Very few full scale installations have been built to treat chemical, semi-chemical, CTMP, bleaching spent liquors & debarking effluents which are considered to be difficult substrates due to the presence of recalcitrant compounds like resins, chlorophenols, tannins etc. In order to improve the biodegradability & reduce the recalcitrance of such waste water streams, there is need to find various alternatives to make these more amenable/susceptible to anaerobic treatment. The literature shows that the possible ways to deal with

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Table-1

Characteristics of Combined Waste Waters From Pulp & Paper Mills

PARAMETER	LARGE MILLS ABOVE 24,000 T/Year	SMALL MILLS UPTO 24,000 T/Year	
		Agro based	Waste paper based
Flow, m^3/t	167-2819 (220)	187-383 (252)	72-159 (107)
pH	6.6-10	6.0-8.5	7.1-7.7
BOD_5 at 20^0C, mg/l	240-380 (295)	220-1067 (698)	100-273 (187)
COD, mg/l	840-1660 (1118)	2120-4763 (2940)	472-876 (654)
SS, mg/l	620-1120 (764)	600-1115 (615)	350-885 (542)
COD/BOD	2.95-4.37 (3.8)	2.49-5.40 (4.2)	2.75-5.7 (3.5)
Pollution load, Kg/T, Paper			
SS	168	155	58
BOD	65	176	20
COD	246	741	70

the recalcitrant compounds is **to adapt microflora, dilute the waste water below threshold level of toxicity, detoxify the waste water by employing chemical, physical & biological methods or use the attached growth reactors instead of suspended growth (McCarty, 1964.).** This necessiates a combination of anaerobic treatment with a pretreatment process to improve not only its biodegradability but to widen the applications of anaerobic treatment to toxic waste waters.

CHARACTERISTICS OF AGRO-BASED PULP & PAPER MILL EFFLUENTS

The high pollution load generated by these mills is primarily due to the absence of chemical recovery system. Thus for producing each ton of paper, the mill generates ~3 times more pollution load than a large pulp & paper mill with chemical recovery. Characteristics of combined waste waters from Indian pulp & paper mills is given in **Table-1**. It is evident from this Table that small pulp & paper mills have a high COD/BOD ratio. The biodegradability & toxicity assay for some of the non-wood fibres is given in **Table-2.**

METHODS OF TREATMENT

It is now well known that many compounds are inhibitory or severely toxic to methanogens. In those cases where the recalcitrant compounds are present in toxic concentration, specific measures have to be taken. In 1964, McCarty first suggested the possible ways to control toxic materials in anaerobic digestion, remove toxic material from waste; dilute the waste below toxic threshold; form insoluble complex or precipitate or antagonize toxicity with another material. Lot of progress & experience has been gained about recalcitrant compounds & their toxic effect on anaerobic digestion & the possiblities for treating toxic wastes. Based on this, the different ways to deal with such toxic wastes are summarised below.

1. **Adaptation of the microflora-Necessity to spend sufficient time to allow the sludge to adapt to the toxic compounds.**

2. **Dilution of the waste water-Applying the dilution of the influent solution to such an extent that the level of toxicity is acceptable &/or that the biodegradation of the recalcitrant compounds proceed without hinderance.**

3. **Detoxification of the waste water-Applying some kind of pretreatment by which the toxic compound is eliminated e.g. a chemical or biological treatment step.**

4. **Avoiding the air oxygen entering the water phase, because for specific waste waters e.g. Potato starch & forest industry it may lead to the formation of severely toxic compounds.**

Table-2			
The Concentrations (IN G COD L^{-1}) of The Various TMP & Soda Pulping Waste Water Resulting in 50% Inhibition of The Methanogenic Activity			
PULPING METHOD	RAW MATERIAL	FIRST FEEDING 50% IC	SECOND FEEDING 50%IC
INDIAN AGRO-BASED FIBRES:			
	Wheat straw	8.0	--
	Rice straw	4.0	10.0
	Bagasse	2.0	5.0

ADAPTATION OF THE MICROFLORA

It has long been a conception that methanogens are far more sensitive to recalcitrant compounds than acidogens & acetogens. But the knowledge & experience gained by the researchers has made the world to reconsider the fact, as from literature reviews it is evident that methanogens have great flexiblity to adapt to a wide variety of toxic compounds if sufficient time is invested on the adaptation to occur. It always is essential to allow the sludge sufficient time for adaptation, even for relatively well biodegradable substrates like a mixture of beer & gelatin. Studies have also revealed that in most cases, the effect is bacteriostatic rather than bactericidal. This very fact opens the avenues for the application of anaerobic treatment to toxic complex waste waters on a commercial scale. The following things are to be taken care of while treating such waste waters.

1. **Anaerobic treatment of toxic waste waters at high loading rate is possible if microflora is allowed to adapt to toxic waste during the start up.**

2. **The load on the reactor should be low enough during the start up of the process, so that the bacteria go through the lag phase during which adaptation takes place & into the exponential phase of unhibited growth & gas production.**

The adaptation period may be longer in many cases depending upon the toxicity of the waste water constituents (even in the range of months), which requires considerable amount of patience when starting up anaerobic processes on toxic waste waters.

DILUTION OF THE WASTE WATER

The concentration of a compound actually determines whether it is inhibitory to the bacteria or not. All chemical substances can become toxic if their concentrations are increased to a certain level i.e above threshold limit. The inhibitory effect may even be reduced if the concentration of a toxic compound is decreased below the threshold limit, & in certain cases it may even stimulate the bacteria. This may be utilised to treat the toxic waste waters by diluting them until the concentration of inhibitory/ recalcitrant compounds are below the threshold limit. The dilution with water will not only reduce the concentrations of substrates but also make it expensive to treat larger volumes of waste water. The dilution method can be of interest in the following case:-

Table-3			
Anaerobic Treatment of Sulfite Evaporator Condensate Bleach Effluents & fs			
	SEC	SBE	SEC:SBE 1 : : 2
COD Loading rate, kgCOD/m^3.day	2.8		5.6
COD Removal, %	68.0	Not	55.0
BOD Removal, %	86.0	Treatable	87.0
Methane yield, m^3/kg COD	0.33		0.33
Acetic acid kg/m^3	0.15		0.06

Table-4

The 50% IC of Hemp Bark & Stem Wood Black Liquor During Sequenced Anaerobic Aerobic Treatment

	50% IC (G COD L^{-1})	
WASTE WATER	BARK BLACK LIQUOR	STEM WOOD BLACK LIQUOR
Untreated	5.9	4.5
Untreated*	6.3	6.4
After anaerobic treatment	11.5	9.9
After Anaerobic/Aerobic treatment	13.5	21.5

* Waste water concentrated by evaporation

1. **When only a minor dilution is required**
2. **When waste water is of a very high strength**
3. **High strength toxic waste water streams can be diluted with less toxic & low strength streams.**

Literature review reveals that the threshold values in certain toxicants need a minor dilution to make the toxic waste waters virtually non-toxic.

The most favourable & ideal condition would be when the toxic waste water can be diluted with another waste water. The situation may further be suitable if the two waste waters have different origin of toxicity/inhibition, in such cases it would be possible to combine them into one non-toxic waste water. In this way a sulfite evaporator condensate & sulfite bleach plant effluent can be combined to be treated anaerobically. Dilution of bleaching waste water from the alkali extraction stage with kraft condensate (Edeline et.al,1988; Qui et. al., 1988) & sulphite evaporator condensate prior to anaerobic treatment is an efficient measure for reducing the methanogenic toxicity. Furthermore, the alkali extraction stage effluents can be utilised to neutralise the acidic sulphite evaporator condensate, which will reduce the cost of neutralisation. The combined bleach effluent could be applied at an organic load of 8-12 g COD l^{-1}-d^{-1}.

DETOXIFICATION OF WASTE WATER

Detoxification of any waste water means that the toxicants are either **eliminated or made inactive** so that methanogenesis could proceed without inhibition. The method to be adopted for detoxification depends upon the type of toxicants present in the waste water. If the characteristics of the inhibitory compounds are known, the possibilitiese of finding a suitable method are much better. The following methods can be used to detoxify a waste water.

Chemical, Physical & Biological

CHEMICAL DETOXIFICATION

Chemical detoxification is usually carried out by precipitating or forming insoluble complexes of the toxicants with certain chemicals having suitable coagulating properties. These chemicals either react, antagonize or precipitate the toxicants. The addition of ferrous ions & its compounds to control/eliminate the sulfide toxicity is a well known measure in anaerobic waste water treatment. Chemical detoxification of CTMP effluent can be carried out by addition of a combination of aluminium, calcium & ferous ions (Welander, 1988). Chlorine & chlorine containing chemicals, especially the metal ions form complexes with the chelating agents like DTPA & precipitates with fatty acids & resin acids. This leads to the major source of toxicity in CTMP effluents. Precipitation as a pretreatment step has been applied to eliminate the toxicity due to long chain fatty acids (Koster, 1987) & resin acids by calcium. These can also be employed to eliminate the toxicity of recalcitrant compounds of lignin (Milstein et.al., 1988).

Laboratory studies conducted at CPPRI, Saharanpur on the precipitation of black liquor of a small papermill based on non-wood fibres with a mineral acid to remove the recalcitrant compounds of lignin improved the biodegradability of the supernatent liquor alongwith COD, BOD & gas production. The results obtained are given in **Table-5** (Gupta, A. 1997). The precipitation processes are associated with the separation of the precipitates & disposal of the generated precipi-

Table-5		
Effect of Lignin Separation on Anaerobic Treatment Efficiency of Black Liquor		
Particulars UOR separating lignin	**Black Liquor**	**Supernatant Liquor At pH 4.5 (after lignin) precipitated**
Amount of gas produced, m^3/kg COD reduced.	0.30	0.40
BOD reduction, %	< 90	> 95
COD recuction, %	<50	>65

tates, which make them technically & economically non-viable.

Another detoxification method was based on the aerobic biodegradation of resin compounds. This observation has led to the development of a detoxification system for CTMP waste waters & Hemp soda pulping waste waters in which the effluent of the aerobic post treatment are recirculated to dilute the influent of the anaerobic reactor (Habets & De Vegt, 1991; Kortekaas, S et.al. 1994).

PHYSICAL DETOXIFICATION

Activated carbon has been used in aerobic waste water treatment in order to reduce the toxic effects of certain compounds by way of adsorption of these toxic compounds which can also be tried either as a pretreatment step or during the anaerobic process. Commercial applications of membrane filteration are in use in Sweden & Japan to detoxify the alkali extraction stage effluents.

BIOLOGICAL DETOXIFICATION

Micro-organisms can degrade/transform many toxic compounds into less toxic compounds. Even if present in inhibitory concentrations, the toxic compounds can be kept at a harmless level in continuous anaerobic systems. The toxicants can be converted into harmless compounds in a separate reactor followed by methanogenesis in another reactor. Separation of anaerobic treatment into two different phases may help in the detoxification of the toxic effluents. The process can be carried out in two phases - an acidogenic, acetogenic phase & a methanogenic phase. The various environmental conditions can be optimised in acidogenic reactor to transform the toxic compounds into less toxic compounds without disturbing the methanogenesis in the subsequent stage.

EFFECT OF REACTOR DESIGN ON THE TREATMENT OF TOXIC WASTE WATERS

FIXED FILM/ATTACHED GROWTH REACTORS

The selection of a suitable reactor design may play an important and crucial role in treating a toxic waste. The advantages of attached growth reactors compared to suspended growth reactors when treating toxic wastes have been shown by the work of Parkin & Speece. (1983). The reasons given by them for the better performance of the attached growth reactors are the following:

- Higher solids retention time, which facilitates the adaptation to occur before wash of the active biomass takes place.
- More plug like flows, which in case of transient toxicity, gives shorter contact times between the biomass & the toxicants.
- In case of chronic toxicity, effluent recycle can be carried to allow for a more gradual exposure to the toxicants.

Further research work conducted on the anaerobic treatment of kraft bleach effluents reveal, the high solids retention time plays a key role in the better performance of the attached growth reactors.

EGSB Reactor design

Recent developments in the high rate anaerobic reactor systems have further opened the potential applications of these processes to deal with the toxic waste waters. The potential advantages of **UASB & FB** have been successfully combined in **EGSB (Expanded Granular Sludge Bed).** EGSB has the following advantages over the conventional UASB:

- High liquid (10 m/h) & gas (7 m/h) upflow velocities.
- High recirculation possible due to the special design of three phase separator.
- Ability to treat low strength, as well as cold & toxic waste waters.

Staged Multi Phase Reactors (SMPA)/ (modular design)

An extremely promising & challenging development for the future & more wider applications of anaerobic systems comprises the **staged multiphase anaerobic (SMPA)** reactor system. This system is presumed to be feasible for all temperature ranges viz. 10 to 55^{0}C and a variety of waste waters, including quite inhibitory compounds of a variety of heavily polluting chemical industries. The SMPA concept have the following basic ideas underlying this modular anaerobic reactor process.

- For many complex industrial waste water effluents, recirculation (upfront) could represent an attractive solution (Kortekaas et.al. 1994).
- Development of the proper kind of anaerobic bacteria in each separate module, depending upon the substrate available & the specific environmental conditions prevailing in the module.
- Prevention of mixing up of the sludge developing in the separate compartments.

Gas produced in the separate modules is prevented from being mixed with gas of the other modules. Aproaching more plug flow conditions in the process, resulting in the higher treatment efficiency.

SPMA concept offers more potentials for the degradation of complex type of waste waters, e.g. comprising inhibitory xenobiotic &/or more or less recalcitrant compounds e.g. different types of aromatics, aldehydes, higher fatty acids etc.

Industrie water Eerbeek in Netherlands is treating waste water of three paper mills in two UASB reactors having modular design.

SULPHIDE REMOVAL METHODS

Methods usually employed for sulphide removal are physico-chemical processes which involve direct air stripping, chemical precipitation & oxidation. However, the methods have the following limitations:

1. The relatively high energy requirements,
2. High chemical & disposal costs make these systems economically non-viable. (Sludge handling problem).

Oxidation processes used for sulphide removal are aeration both catalysed & uncatalysed, chlorination, ozonation, potassium permangnate & hydrogen peroxide treatment. In all these oxidation processes sulphur, thiosulphate & sulphate may be the end products.

Biotechnological Methods

Since physico-chemical methods have limitations, the development of biological method for the removal of sulphide may be of immense importance.

A major breakthrough has been achieved in the recovery of elemental sulfur by the use of thiobacilli under controlled Oxygen conc. during the reduction of sulphate to H_2S/S^{-2} at Agricultural University of Wageningen, The Netherlands. The biological removal would not only protect environment but also preserve the resource.

The process has been commercialised by Paques B.V. and is in operation at Industrie water Eerbeek in Netherlands which is treating the waste water of three paper mills. The bioscrubbing has resulted in 99.99% removal of hydrogen sulphide.

Although, anaerobic treatment can remove most of the BOD i.e. above 90% in many cases & many low molecular weight compounds that are acutely toxic in anaerobic environment, a large part of COD will still remain in the treated effluent. These recalcitrant/refractive/non-biodegradable, mainly high molecular substances cause the dark colour of the effluents. In order to remove/eliminate these compounds to improve the COD removal, the anaerobic tratment has to be combined with some other treatment. Although, most of the pulp & paper mill effluents toxic to be treated anaerobically, in many cases the toxicity can be controlled or overcome if the problem is dealt in a proper manner. In most of the cases anaerobic treatment itself is a pretreatment process which requires further treatment of anaerobically treated effluents before being disposed to surface water.

CONCLUSIONS

Although pulp & paper mill effluents contain recalcitrant compounds, these can be made amenable to anaerobic treatment by combining a suitable pretreatment process.

The various pretreatment options may be adaptation of microflora, dilution & detotxification of waste waters & the choice of a suitable reactor design.

Sufficient time must be given for the adaptation of the microflora.

Dilution to subtoxic levels should be applied where ever possible.

The possiblity of the first two options can be evaluated by conducting laboratory experiments in the serum bottles. The possiblity of using the third option should be tried in a continuous process. If the first two options do not fulfill the requirement are not feasible the third option i.e. a suitable detoxification method must be found & tried.

Before evaluating any suitable detoxification process, the composition of the waste water must be studied extensively alongwith the various characteristics as well as their biodegradability under anaerobic conditions. Based on this, the possiblities of detoxifying the waste water by various physico-chemical & biological methods can be evaluated.

The fourth option may be the choice of such a reacor design which facilitates the removal of toxic pollutants like fixed film reactors instead of attached growth reactors & improved versions of high rate anaerobic reactors like that of UASB e.g. EGSB. The use of Staged multiphase anaerobic (SMPA) reactor system.

Anaerobic treatment of sulphur containing waste water requires a post treatment to improve the environment. The treatment is not carried out to use the biogas as a fuel but it is mandatory to keep the levels of hydrogen sulphide below toxic levels.

Anaerobic treatment of toxic waste waters necessiates the combination of anaerobic treatment with a pretreatment process to remove recalcitrant compounds.

Anaerobic treatment in most of the cases may be a pre-treatment step which requires a post treatment before the anaerobically treated effluents are discharged into the surface waters. Aerobically treated effluents may be used for upfront dilution to reduce the conc. of recalcitrant compounds.

The development of such combined treatment processes may be of immense importance for small pulp & paper mills in the country, which will not only be benifited by the generation of biogas but also reduce the pollution load, which otherwise will effect the very survival of the mills with increasing stringent environmental laws.

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