

HYDROGEN PEROXIDE - A QUICK SOLUTION TO RECTIFY FOUL CONDITIONS IN ACTIVATED SLUDGE PROCESS



Kishore Chandra Choudhury

Freelance Consultant, 302, Sri Srinivasam Apartment, KDR Colony,, Madinaguda, Miyapur, Hyderabad-500049.

Abstract:

Green manufacturing or 'greening' of manufacturing means **use fewer natural resources, reduce pollution and wastage, recycle and reuse materials and moderate emissions** in the process. Basically, it is to preserve the natural resources and to return it to nature in its best condition, if consumed. Out of all the above said dimensions of green manufacturing "Reduce Pollution" is one of the important dimensions. In paper industries one of the natural resources consumed in high amount is water. And it generates high amount of effluent (waste water / polluted water) to be returned to nature (river or Nalla). This creates a big threat to water bodies.

Government has implemented stringent regulatory norms for industrial and domestic effluent treatment plants to control stream pollution. Most of the industries have installed robust greening technologies to achieve all the norms laid by the regulatory authorities. Activated sludge process is one of the popular treatment processes adopted by many paper industries. Due to high stringent norms, they are walking on the edge. So, any moment the desired properties may slip off the norms and foul conditions may come on the path due to temporary overload or equipment failure. At this juncture, it is very difficult to make it up, to achieve the norms again. Sustainability has a question mark here.

At this crucial point, hydrogen peroxide (H_2O_2) worked as a soothing medicine though it is a highly corrosive and oxidative chemical for microorganisms present in the activated sludge process. In general, H_2O_2 is a strong oxidizing agent and used as a disinfectant / germicide. Besides this, it has other properties like source of nascent

oxygen, converting odorous sulfides to odorless sulfates, which helped in controlling the foul situation. It acted as the best SOS medicine for fouled aeration basin.

To achieve the positive activities of H_2O_2 in activated sludge process, the critical process parameters like optimum dosing point, optimum dose & concentration, duration of treatment are discussed. If not used properly, it could be more detrimental to the foul situation.

Besides this, the chemical reactions of H_2O_2 in activated sludge process are explained. The impact of H_2O_2 on dissolved oxygen (D.O.) at aeration basin and impact on BOD, COD & D.O. in final effluent discharge are discussed.

Introduction:

Environment, resources and population are three main problems faced by the world today. Environment is crucial one with and change in climate at any point leads to the imbalance of the earth. The deteriorating environmental problems have posed a serious threat to human survival and development. The waste in the manufacturing process, i.e., transforming resources into products leads to serious environmental pollution. Hence green manufacturing is a modern manufacturing model considering both environmental impact and resource efficiency under the premise of guarantee the quality, the features and the cost of the product. Make the products such that there is lowest environmental impact in the whole product life cycle, so that the resource utilization rate is the highest and energy consumption is the lowest. With the rapid development of the manufacturing industry, environmental issues have become increasingly prominent and become the attention focus of all the countries. The "green wave" makes the manufacturing industry change the traditional manufacturing mode and promote green manufacturing technology.

Besides wood as the main raw-material for paper manufacturing, the other natural resource consumed in high amount is water. In green manufacturing, this resource (water) has to be used optimally and the waste water generated from the manufacturing process must be treated properly to be recycled, reused and or returned to nature with minimized environmental impact. The treatment system must be foolproof to absorb all shocks of process variations and operational mistakes. Many paper industries are leaving on the edge at this point. The targeted norms may slip off any moment without any sign. Once it goes out, very difficult to restore immediately.

Most of the paper industries practice activated sludge process to treat waste water as organic load is more in paper mill waste water. Activated sludge process is one sort of cultivating aerobic microorganisms; those eat away organic wastes from effluent. Hydrogen peroxide (H_2O_2) is an oxidizing agent sometimes used as micro-biocide and also a source of oxygen to feed microorganisms. This paper describes the use of

hydrogen peroxide in activated sludge process as an oxygen source and to balance the process shocks to make it foolproof.

ACTIVATED SLUDGE PROCESS:

Basically effluent treatment processes are divided in to two major categories - Aerobic and Anaerobic treatment. Where the organic load is less and the influent volume is high, aerobic process is practiced and where the volume is less and pollutant load high, anaerobic process is practiced. Activated sludge process comes under aerobic treatment method.

Steps of aerobic treatment process:

- 1: Screening and Pumping. ...
- 2: Grit Removal. ...
- 3: Primary Settling. ...
- 4: Aeration / Activated Sludge. ...
- 5: Secondary Settling. ...
- 6: Filtration / Oxygen Uptake pond

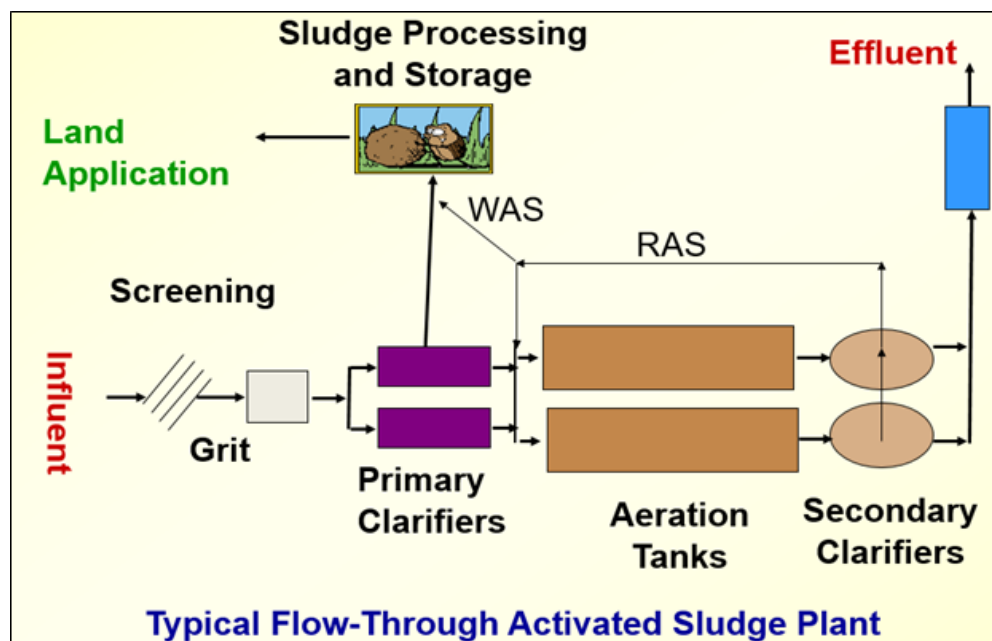


Figure 1

The term activated sludge refers to suspended aerobic sludge consisting the flocs of active bacteria, which consume and remove aerobically biodegradable organic substances from screened and pre-settled waste water. Generally activated sludge reactors are open tanks / basins where waste water is mixed and aerated by pumping air or oxygen in to the tank or by surface aerators. The microorganisms oxidize the organic carbon in the waste water to produce new cells[1], carbon dioxide and water. Although aerobic bacteria are most common organisms, facultative bacteria along with higher organisms can be present.

Organic material + O_2 + nutrients \rightarrow CO_2 + H_2O + New Cells + nutrients + Energy

Besides the above bio-chemical process, another goal is **Nitrification/Denitrification** in activated sludge treatment[2]. **Nitrification** is an aerobic process happening in aeration lagoon, in which bacteria oxidize the reduced-forms of nitrogen. **Denitrification** is an anaerobic process occurring during secondary clarification by which oxidized forms of nitrogen are reduced to gaseous forms, which can then escape into the atmosphere.

Nitrification: $NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^-$ & $NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$ (ammonia to nitrite and then nitrate)

Denitrification: $\text{NO}_3 + \text{R-OH} \rightarrow \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O} + \text{OH}^-$ (nitrates are reduced to Nitrogen gas & escapes to environment)

The flocs, which form in the aerated tank, can be removed in the secondary clarifier by gravity settling. Some of this sludge is recycled back to the reactor (aeration tank) as seeds. The treated clear effluent with standard TSS, COD, BOD and DO can be discharged in to the river or treated in a tertiary treatment facility if required for further use. For agricultural use, it is not necessary to remove all nutrients[3]. For recycling in paper industries further treatment is done to remove hardness (dissolved solids) and adjust pH.

FOUL CONDITION IN ACTIVATED SLUDGE PROCESS:

Fouling can generally be divided into four categories: chemical fouling, biological fouling, deposition (or sedimentation) fouling, and corrosion-fouling. Here, it is discussed only about biological fouling and sedimentation fouling. Biological fouling is the accumulation of microorganisms on wet surface and deposited / sedimented at bottom of the surface. Activated lagoon works on this biofouling principle that microorganisms consume oxygen and convert dissolved organic material into active biomass. But the basic requirement here is that this mass must be in suspended form and removed by sedimentation method in another basin/ clarifier leaving the clean water for further use or draining to other water bodies.

The foul condition comes when they make a biofilm and settle at bottom of the lagoon. Hence they do not get enough oxygen and anaerobic activities start by facultative microorganisms. Or if at all, they are in suspended form, but enough oxygen is not available for catabolic respiration, anaerobic activities start. Instead of oxidizing, reducing biochemical reactions start. Sulfates are reduced to sulfides and H_2S and SO_2 are generated and a foul smell (rotten egg smell) indicates failure of activated lagoon process. If nitrates are reduced to amines / ammonia, then a fishy smell comes from lagoon. Earthy smell indicates good health of lagoon.

CAUSES OF FOUL CONDITION:

The common causes are:

1. Organic overloading.
2. Short circuiting or short hydraulic detention.
3. Overgrowth of SRB.
4. Old sludge accumulation.

5. pH shock
6. High temperature and or temperature shock.
7. Partial nitrification.

The above all points are inter-related. They may make the situation complex. When organic overloading happens, the dissolved oxygen (DO) depletes and F/M ratio reduces. Once DO depletes, the filamentous bacteria like *Nocardia* and *Microthrix parvicella* and other non-aerobic bacteria grows in high rate. Hence, thick foam is observed in aerated tank and bulking of sludge occurs. Bulking creates other problems in secondary clarifier. Further, sulfur reducing bacteria (SRB) grow in low DO environment and start anaerobic activities. They reduce sulfates to sulfides. Foul smell comes from it. To overcome this bulking more and more sludge is wasted, so short hydraulic retention occurs. Then young cells may be more which will not settle. Next, increased sludge retention time and reduced wastage is to solve it. So, old sludge accumulation is done. One after other, all problems come together and make it complex. Low pH[4] or pH shock and temperature changes adds fuel to the problem. At this juncture controlling low DO is very very difficult. Here comes H_2O_2 as SOS (save our souls) medicine.

CASE STUDY ON SOLVING FOULED ACTIVATED SLUDGE PROCESS:

One of the client paper mills having multiple paper machines, no pulp mill but one recycled fiber deinking plant faced the issue of low DO, then strong foul odor and all other complexities of bulking, foaming & settling issues. Tried to solve this with different options and finally achieved with hydrogen peroxide.

Sketch of ETP set-up at plant:

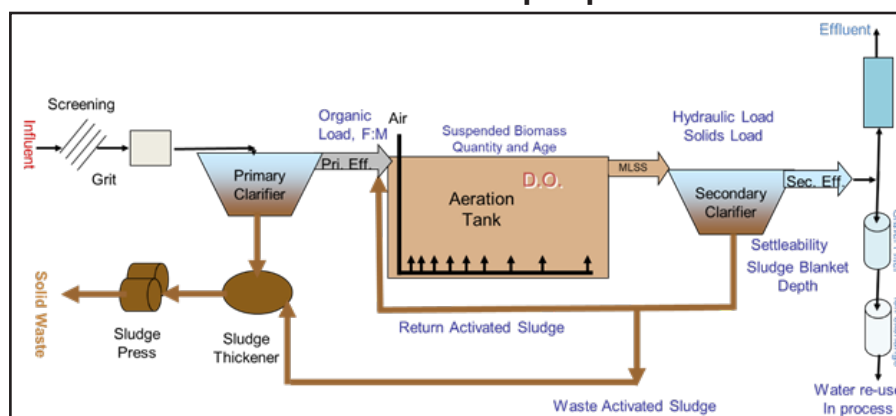


Figure 2

Normal performance plant data:

Plant was running normal and meeting the norms set by pollution control board. The normal operation data is given in Table-1.

Sl. No.	Control Parameters	UOM	Entry 1 ^o clarifier	Exit 1 ^o clarifier / Entry Aeration Tank	Effluent Exit 2 ^o clarifier	Aeration tank
1	TSS	mg/l	2885 (1540 – 3460)	190 (105 – 300)	67 (36 – 90)	
2	COD	mg/l	2490 (1216 – 3164)	513 (280 – 650)	153 (66 – 200)	
3	BOD	mg/l	1159 (670 – 1490)	262 (176 – 310)	22 (13 – 28)	
4	pH	-	6.6 - 7.0	6.8 - 7.2	7.1 - 7.3	
5	DO	mg/l				0.7 (0.4 - 2.8)
6	MLSS	mg/l				1700 (1520 – 1860)
7	MLVSS	mg/l				1213 (1098 – 1365)
8	MLVSS/MLSS	Ratio				0.71
9	COD removal	%				70.2
10	BOD removal	%				91.6

Tabl-1 Data during normal operation before trouble

Activated sludge failure / fouled condition:

One day the DO started dropping from 2 mg/l and reached 0.2mg /l at the day end. The Plant had the diffuse aeration system and it was running one air blower. The second standby blower was started to increase the DO value. But it does not make any significant change, DO improved slightly.

COD was observed high in influent (>4000 ppm), anticipated that BOD would be higher though the result would come after 5 days. To maintain the F/M ratio, the MLSS wasting reduced and return activated sludge (RAS) increased. But there was no improvement. Rather it was detrimental as more food and more microorganisms present in aeration tank and shortage of oxygen. The DO again went down to 0.2 mg/l.

In two days, rotten egg smell started from aeration tank indicating septic conditions and growth of sulfur reducing bacteria (SRB). Microscopic observation of activated sludge confirmed, presence of filamentous bacteria (Nocardia, Microthrix & Type1863 etc.). They are shown in Figs - 3 to 6. Brown foam observed in aeration tank and sludge bulking followed. Poor settling happened in secondary clarifier. The final effluent was about to cross the norms. The MLSS in aeration tank turned blackish with objectionable foul smell.



Figure 3



Figure 4

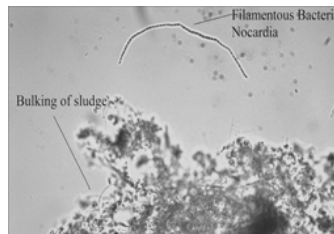


Figure 5



Figure 6

Then wasting of activated sludge (WAS) increased and pumped to sludge thickener and solid waste line to reduce septic MLSS from the system. So cow dung was added to aeration tank as fresh cells to control bulking. Cow dung was not a quick solution to control the situation. It would take long time to replace MLSS with new cells. And new cells would not settle easily. Besides this, problem started at sludge thickener and belt press to remove solids. There was no improvement in DO at aeration tank. The control data during this problematic period is given in Table 2.

Sl. No.	Control Parameters	UOM	Entry 1° clarifier	Exit 1° clarifier / Entry Aeration Tank	Effluent Exit 2° clarifier	Aeration tank
1	TSS	mg/l	4863 (3554 – 7260)	256 (174 – 364)	113 (92 – 160)	
2	COD	mg/l	3462 (2741 – 4060)	667 (548 – 802)	219 (193 – 249)	
3	BOD	mg/l	1365 (1110 – 1670)	275 (257 – 310)	38 (34 - 40)	
4	pH	-	6.7 - 7.0	6.9 - 7.2	7.1 - 7.4	
5	DO	mg/l				0.2 (0.0 - 0.2)
6	MLSS	mg/l				2240 (1758 – 2852)
7	MLVSS	mg/l				1130 (881 – 1386)
8	MLVSS/MLSS	Ratio				0.50
9	COD removal	%				67.0
10	BOD removal	%				86.1

Table-2 Data during troubled period

At this situation, thought to add chlorine, or sodium hypochlorite to aeration tank to kill SRBs/filamentous bacteria. Added a small quantity of sodium hypo with fear that it could destroy all the microbes. Then proposed to add hydrogen peroxide (H_2O_2), it will kill SRB and simultaneously give oxygen[5] on decomposition of it. Still it was very risky as H_2O_2 may act as a biocide.

H_2O_2 dose and dosing point step by step attempts:

Planned to dose at the secondary clarifier central well where MLSS is pumped for clarification. But the clarifier design was such that the platform was moving along with the sludge scraper of the clarifier. There was practical difficulty in putting the pipeline for H_2O_2 dosing. Hence, there was a thought for alternative dosing point. Team suggested to put one PVC pipe deep in to the aeration tank bottom near the diffusers and dose H_2O_2 near the diffusers to generate oxygen there itself. Accordingly, this was made and H_2O_2 dose started at a low dose @ 2 mg/l with a fear of spoiling the MLSS. No change observed. After 4 hours, dose increased to 5 mg/l. Step by step, H_2O_2 dose was increased to 25 mg/l. No impact was observed.

Then dosing point was changed to aeration tank overflow launder. There also, no impact was visible. Then, again thought of secondary clarifier central well. As it was not practicable, planned to dose at MLSS pump inlet. There was an open pit, from which pumps were pumping to secondary clarifier central well. H_2O_2 dosed at that point @ 10 mg/l and slowly increased to 20 mg/l. Some sludge bundles are coming up and

floating in secondary clarifier. But the water looked clear (not turbid) in the launder. Besides, some floating mass was there in the sludge settling well. After few hours, the floating mass disappeared. H_2O_2 dosing was continued and after 8 hours the dose increased to 30 mg/l. It was observed that the secondary clarifier behaved well and clear water was coming to launder. It was continued the same overnight. Next day, no foam was observed in the aeration tank, there was no septic odor and the colour of MLSS changed from blackish to brown.

The control parameters achieved after optimizing the dose of H_2O_2 are given in Table 3.

OPTIMIZED H_2O_2 DOSING POINT AND DOSE:

The hydrogen peroxide dosing point was optimized and finalized to be at MLSS feed pit of secondary clarifier. The dose was further increased to 40 mg/l. Good results were observed. COD, BOD, TSS, DO and other properties came to normal operation in one day. It was concluded that 40 mg/l or may be little more could be safe dose of peroxide at this dosing point without hindering the microbial growth.

The DO trends in aeration tank in normal run, problematic period and while running H_2O_2 are given in Fig-7. The COD and BOD trends at secondary clarifier overflow during these periods are given in Fig-8 and Fig-9, respectively. During hydrogen peroxide run, there was an improvement in COD removal[6] percentage by 2.6 points at aeration tank as compared to normal run. BOD removal percentage improvement was marginal as the BOD entry to aeration tank was less as compared to normal period (Ref: Table-1 and Table-3).

Sl. No.	Control Parameters	UOM	Entry 1° clarifier	Exit 1° clarifier / Entry Aeration Tank	Effluent Exit 2° clarifier	Aeration tank
1	TSS	mg/l	4112 (2108 – 5860)	82 (44 – 89)	53 (33 – 104)	
2	COD	mg/l	3697 (4114 – 5400)	361 (287 – 512)	98 (82 – 128)	
3	BOD	mg/l	767 (640 – 1021)	183 (140 – 253)	15 (10 – 22)	
4	pH	-	6.7 - 7.2	6.5 - 6.8	6.8 - 7.1	
5	DO	mg/l				1.4 (0.6 – 2.3)
6	MLSS	mg/l				1570 (1160 – 1987)
7	MLVSS	mg/l				1320 (1028 – 1622)
8	MLVSS/MLSS	Ratio				0.84
9	COD removal	%				72.8
10	BOD removal	%				91.8

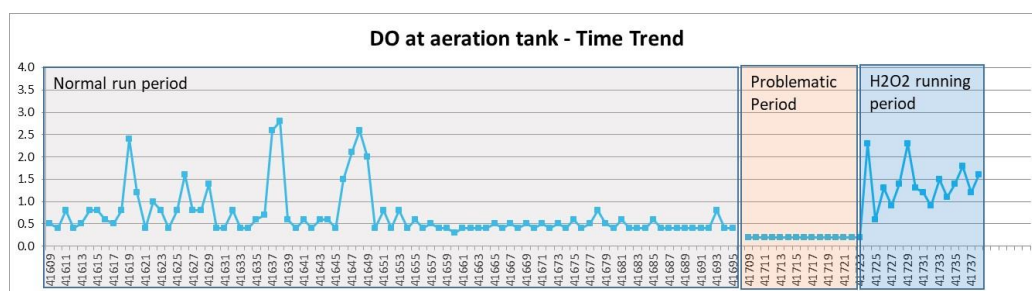
Table-3 Data after trouble shoot out (during H₂O₂ dosing)


Figure 7

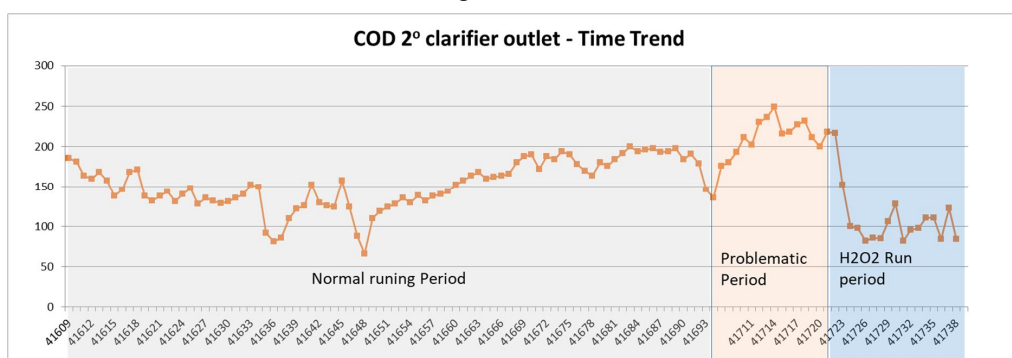


Figure 8

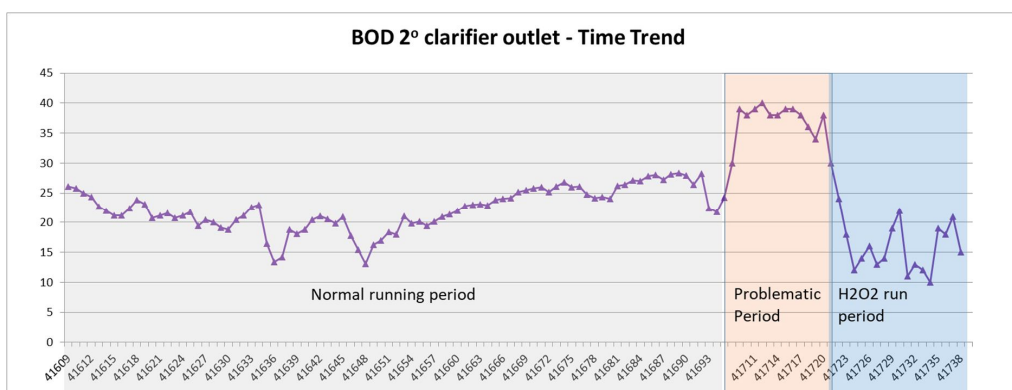
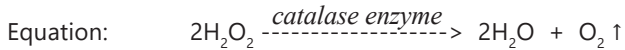


Figure 9

Nguyen et al. (2015) said in their research paper[7] that 50 mg/l H_2O_2 dose was optimum for oxygen uptake rate (OUR), 100 mg/l was good for COD removal and there was no harm to microorganisms up to 150 mg/l of H_2O_2 . But these may vary according to pH and temperature. Optimum pH was 6-8 and optimum temperature was 25-30°C.

CHEMISTRY OF H_2O_2 :

Hydrogen peroxide is not stable. It decomposes to water and oxygen once the seal of the container is opened and the reaction is catalyzed in presence of metal ions like iron, manganese, lead etc. It is also catalyzed by catalase enzyme produced by almost all common microorganisms. In waste water, it is available in plenty. There was no need to add iron salts[8].



Molecular wt.: 68.02936 g -----> 36.03056 g + 31.9988 g

Percentage (%): 100% -----> 52.96% + 47.04%

Oxygen (O_2) generated is 47.04% from one mol of H_2O_2 . In 50% H_2O_2 concentration, the oxygen availability is 23.52%.

H_2O_2 is available in different range of concentrations. For industrial application, it is available in 27%, 35%, and 50%. Net oxygen availability from different strength of H_2O_2 is given in Table-4.

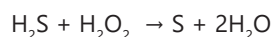
H_2O_2 solution strength	3%	27%	35%	50%
O_2 availability % in solution	1.41%	12.70%	16.46%	23.52%
Specific Gravity (SG)	1.0059	1.10	1.13	1.20
H_2O_2 g/l	1008.94	1098.81	1128.77	1199.46
O_2 , kg/l	0.014	0.140	0.186	0.282
O_2 , g/l	14	140	186	282

Table-4 Oxygen availability in different strengths of H_2O_2

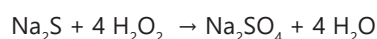
The H_2O_2 dose determined on the basis of the availability of O_2 in solution. It is calculated according to the said chemistry.

Hydrogen sulfide is a frequent wastewater contaminant because of the conversion of sulfates to hydrogen sulfide by bacteria under anaerobic conditions. This is a particular problem during summer months and/or during periods of high BOD/COD loading, when the oxygen demands of a system are exceeded, resulting in septic conditions.

Hydrogen peroxide reacts with hydrogen sulfide under acid, neutral and alkaline conditions.[9] The reaction is accelerated by increasing temperature and/or the addition of catalysts such as iron. The stoichiometry is also affected by pH. Under acidic or neutral conditions, the reaction with hydrogen peroxide produces sulfur and water:

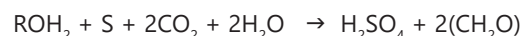


Ideally, hydrogen peroxide at acidic/neutral pH, reacts mol for mol with hydrogen sulfide; however, since waste streams often contain other reactive materials, it may be necessary to add more than the stoichiometric amount of hydrogen peroxide. In alkaline solution (> pH 8), the dominant reaction is:



The 4/1 molar ratio of H_2O_2 /sulfide can be lowered by using a combination of air and hydrogen peroxide.

Besides this, there could be sulfur oxidizing bacteria like Thiobacillus, Thiothrix and Beggiatoa. These bacteria oxidizers survive by detoxifying H_2O_2 produced metabolically.[10] These convert sulfur in to sulfates like sulfuric acid and lower the pH. This may be the reason the pH observed low during H_2O_2 dosing period. pH may be improved in presence of Fenton's solution[11].



These sulfur oxidizing bacteria like Beggiatoa (filamentous) consume 85% of oxygen due to sulfide oxidation[12] and only 15% are consumed by rest of the microorganisms. This increases the oxygen consumption. But presence of these bacteria is very rare in paper mill effluent system.

CONCLUSIONS:

Hydrogen peroxide proved to be the best solution to get out of septic conditions very quickly (less than 8 hours). Up to 100 mg/l of H_2O_2 can be dosed to the activated sludge system without any fear of inhibition to microorganisms. At this safe dose, H_2O_2 does not inhibit or kill the microorganisms, but chemically reacts and oxidizes sulfides, sulfites and thiosulfates to sulfates which are odorless. Besides this, it increases DO level in the aeration tank, which inhibits SRBs (sulfur reducing bacteria) those reduce the sulfates. Hence H_2O_2 is a SOS medicine for fouled activated sludge process. One cannot take risk in green manufacturing

process and should have the H₂O₂ dosing system ready. Though it is costly, it will be the way in future.

H₂O₂ may be used regularly along with diffused aeration or surface aeration to upkeep good health of activated sludge tank/ aeration tank by maintaining optimum DO. Simultaneously, it reduces COD and BOD from the effluent. But the cost of operation is high as compared to mechanical aerators.

H₂O₂ may be used as pre-treatment before activated sludge, where the COD is very high and comparatively low volume of waste water, to oxidize complex organic matters to simpler biodegradable material, which can be processed easily in the activated sludge process.

For recycling of treated water in manufacturing system, H₂O₂ is used as a pretreatment before gravel filter and ion exchange. Maximum water can be reused in process again. 100% of treated water can be used for agriculture as toxicity is reduced by H₂O₂.

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