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TACKLING WATER CONTAMINATIONS BY $CL0_2$ TECHNOLOGY

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Abstract:

This paper deals with the treatment of "Process Contaminations" like slime & odour problem with "ClO_2 technology" which is caused by excessive water recycling. If process water is circulated without proper treatment, interfering substances such as anaerobic & aerobic microbial counts, slime, deposits to cause technical & commercial problem, hence productivity loss.

ClO_2 is a novel technology to offer cost effective solution. As ClO_2 can't be transported and has to be generated onsite. We will explain the model to generate it onsite. There are multi-pumps methods of ClO_2 reactor.

As this technology is running successfully in few mills across India, we will discuss one of the case studies, which has benefited by using this technology.

Keywords: Closed water circuits, Slime, Odour control, ClO_2 reactors, Case Study

Introduction:

Water resources are limited and to be used with responsibility as ground level availability data are alarming. In Indian contest, 17% of world population is dependent on 3% of ground water [R1]. Hence serious efforts are being made to deal with this scarcity from all sections.

Industries too have taken the challenge positively for sustainable growth & to fulfil its environment commitments and encouraging more & more treated water use, back to process, so that natural water can be used for only application it should be - drinking .

But the counterproductive aspects are - increased inorganic & organic loads due to high molecular weight organic acids, heavy metals, iron & phenols, sulphate and carbonates. These negative substances contribute increased TDS, huge biological loads in terms of BOD/COD, hardness and alkalinity, etc. [2]

ClO_2 being a selective oxidiser proved to be economical solution to deal with. Now with innovation of onsite ClO_2 generation has made it possible to implement this useful technology.

MATERIALS & METHODS

Latest state of art chlorine dioxide generator (design details in Table 1 and Fig. 1) generates point of use chlorine dioxide using pure form of 10% sodium chlorate and diluted hydrochloric acid (10%) or sodium hypo or chlorine.

Reaction Chemistry

$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O$

Table 1: *Design details*

Volume of water to be treated	50-300 m³/h
Capacity of ClO_2 generator required	500-2000 g/h
$NaCl0_3$ (25%) required	5.2 lph
HCl (10-11% conc.)	5.2 lph
Drive water flow rate	450 lph

Fig. 1: Chlorine dioxide generator

Major Contaminations

Slime/ deposits, odour, blackish color and microorganisms cause technical & commercial loss to mill at later stage if not treated at its sources.

Slime is formed due to polymer and slime activators. Natural & synthetic polymers such as polyvinyl acetate/acrylamide and slime activators like borate ion makes cool sticky substances which may get accumulated in Head box/ screens and choke the showers and may also create paper holes & poor machine runnability, if picked by felts.

Majorly, four types of bacterial growth namely Pseudomonas, Kiebsiella, Enterbactor and Bascillus takes place [3].

Aerobic respiration generates more TPA than fermentation of anaerobic respiration, which can be used or stored for later uses. This changes the metabolism of molecule. Thus making solution anoxic and release of intermediate gases like H_2S, mercaptans and other organic acids. This majorly contributes to odour. At the same time, dissolved iron turns the water dark in case of cutting of oxygen flow.

Monitoring and Control

- ✓ ORP or redox (Oxidation reduction potential)
- ✓ CFU (Microbial counts)
- ✓ VFA (Volatile fatty acids)

Chlorine dioxide: is an efficient biocide recognized for its disinfectant properties. In 1988, EPA registered chlorine dioxide gas as a sterilant.

Properties: Chlorine dioxide in the gaseous form is yellow in color. In the liquid state it is red in color. Chlorine dioxide is easily soluble in water. The solubility depends upon the partial pressure of chlorine dioxide and solution temperature.

Chlorine dioxide gas is very reactive and unstable and hence it cannot be transported. However, in aqueous solutions at low concentration it is stable as a dissolved gas. Hence, it is normally used as a weak solution in water and must be produced onsite using a generator.

It is an excellent micro-biocide. The chlorine dioxide penetrates and ruptures the bacteria cell wall and reacts with vital amino acids in the cytoplasm of the cell, thus killing the organisms.

Chlorine Dioxide Mode of Action

The anti-microbial activity of chlorine dioxide is extremely broad spectrum. It is highly effective against gram negative and gram positive, aerobic and anaerobic, spore forming and non-spore forming pathogenic and saprophytic bacteria.

In general, microbes have two differing cell types, prokaryotic and eukaryotic structures. Most bacteria have the more simplistic prokaryotic cell type, where enzymes are located just inside the cellular membrane. These locations come under oxidative attack almost immediately from chlorine dioxide and therefore these cell types are most rapidly destroyed. Fungi and protozoa are of the eukaryotic cell type, where their enzyme systems are located deeper within the cell structure and therefore are slightly more resistant to rapid destruction. Bacterial spores have many layers of protective material surrounding them and therefore are more resistant. For example, a vegetative bacterial cell may require only 30 seconds exposure to chlorine dioxide for cell death to occur, while its spore form may require 5 minutes. Fungal spores are not nearly as protected as bacterial spores and show very little resistance to chlorine dioxide.

Why Chlorine Dioxide is preferred Disinfectants

- There is no significant formation of tri-halomethanes (THMs).
- It does not react with bromides to form bromine or bromate (which is a known human carcinogen) or promotes the formation of other brominated hydrocarbons.
- It does not react with ammonia and is only slightly reactive with primary amines.
- It does not chlorinate fatty acids to form haloacetic acids (HAAs) at normal dosing concentrations.
- Effective over wide pH spectrum range 3-11; hence lower consumption.
- Used for pre-treatment due to selective reactivity with iron/ manganese.
- Hydrolyses sulphide to act as odour control.
- Penetrates and destroys biofilm to be more effective biocide.

ClO_2 Selectivity

- Iron & manganese precipitates have to be filtered
  - 1 mg iron consumes 1.2 mg of ClO_2.
  - 1 mg manganese consumes 2.5 mg of ClO_2.
- Nitrite is oxidised to nitrate, sulphide to sulphate & sulphur.

- 1 mg nitrite consumes 2.9 mg of CLO_2
- 1 mg sulphide consumes 2.1 mg of CLO_2

Excellent waste water treatment option for algae bloom control & odour control.

Chlogen Generators

The unique generator design ensures highly efficient generation of chlorine dioxide. It is available in panel mount as well as in skid mounted design along with accessorial dosing pumps incorporated in the unit for dosing all the above mentioned chemicals.

Unique Feature

- On-site ClO_2 generation for immediate use.
- ClO_2 can be injected directly to the treatment system.
- No loss of efficiency with variable flow.
- Flooded reactor design for added safety.
- Available control mode: Flow Proportional, Batch Mode, Residual Trim
- IOT support for data visualization, Remote monitoring and Control, Process automation and auto email alert through Fluent

CASE STUDY

The mill data from one of the case studies of a mill producing brown paper @ 400 TPD are given in Tables 2 and 3.

CONCLUSIONS

Onsite generation of chlorine dioxide has made it possible for the mills to utilize unique features of reagent to treat contamination, which interfere the process negatively otherwise. Technology is affordable tried & tested. There are many references across India operating at different tropical conditions and ground water quality.

Space requirement for reactor is small and it can be installed close to dosing point or even above the tank. It's safer, simpler, effective and most importantly cost effective.

Table 2: *Mill study data*

Cl02 dose	Dosing Point	LAB	Date	Sample code	Aerobic		Anaerobic		VFA
LPH					CFU/ml		CFU/ml		mg/l
3	Clarified water tank	CSIR Report	Before ClO_2 start	DAF outlet	2800000	2.8X10*6	300000	3X10*5	32179
3		CSIR Report	12-10-22	DAF outlet	2400000	2.4X10*6	10000	1X10*4	27273
3		CSIR Report	01-11-22	DAF outlet	4800000	4.8X10*6	30000	3X10*4	41080
6		IEI Report	08-11-22	DAF outlet	640000	6.4X10*5	65000	6.5X10*4	
6		IEI Report	22-11-22	DAF outlet Before	200000	2X10*5	140000	1.4x10*5	
6		IEI Report	22-11-22	DAF Outlet After	170000	1.7X10*5	31000	3.1x10*4	
6		CSIR	29-11-22	DAF Outlet	4400000	4.4X10*6	30000		34973
6		CSIR	19-12-22	Paper Sample		3x10*3		31x10*6	
6	Top and bottom silo - split dose	IEI	24-01-23	Top Silo	1230000	1.23x10*6	700000	0.7x10*6	15352
6		IEI	24-01-23	Bottom Silo	340000	0.34x10*6	380000	0.38x10*6	13683
6		IEI	24-01-23	Paper Sample	1430000	1.43x10*6	160000	0.16x10*6	
6		Veatch Chennai	24-01-2023	Paper Sample		50X10*3		9X10*3	
6		Veatch Chennai	24-01-2023	Top Silo	6200000	6.2X10*6	80000	80x10*3	37428

Table 3: *Data on paper VFA (mg/l)*

PPAER SAMPLE									
Date	Lab	VFA		Date	Lab	VFA		Date	Lab	VFA
19'Dec22	CSIR	737		13'Jan23	Mills	742		24'Jan23	IEI	1390
1'Jan23	Mills	542		17'Jan'23	Mills	720		24'Jan23	VItech	543
13'Jan23	IEI	550		20'Jan23	Mills	691		28'Jan23	Mills	657

References:

1. Central Ground Water Board (CGWB), Ground Water Year Book, India 2010-11.

2. Renu Saraf, Adv. Training of Water Chemistry (ppt), Ion Exchange (I), Mumbai, 2021.

3. S. Sood & C. Sharma, Bacteria in Indian food packaging paper & paperboards with various contents of fiber. Food and Nutrition Sciences 10(4), 349-357 (2019).