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Micronutrients Technique (MNT) with Constructed Wetlands (CWs) at CTM Jiangmen Waste Water Treatment Plant

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Abstract: ***Constructed Wetlands (CWs) and Sludge Drying Reed Beds (SDRBs) technique is often applied in small scale municipal wastewater sludge reduction or storm water treatment. There are very few case studies in using this technique at the industrial scale. The purpose of this study is to find out the wastewater treatment effectiveness of Micronutrient Technique (MNT) combined with CWs in this special paper manufacturer at the city of Jiangmen, Guangdong, PRC. This experiment and the results have been found that MNT and CWs combined process can be used to improve the efficiency of this industrial wastewater treatment plant.***

Keywords: MNT, Micronutrient Technique, CWs, Constructed Wetlands, SDRBs, Sludge Drying Reed Beds, COD, Chemical Oxygen Demand, BOD_5, Biological Oxygen Demand for 5 days, TSS, Total Suspended Solid, TP, Total Phosphorus, NH_3 N, Ammoniacal Nitrogen

1. Introduction

China Tobacco Modi (Jiangmen) Paper Co., Ltd. (CTM) is a joint venture established by China National Tobacco Corporation and Schweitzer-Modi International (China) Co., Ltd., each with a 50% share (*Jnyawei.cn., 2018*). China National Tobacco Corporation is the main operating company under the State Tobacco Monopoly Administration, responsible for leading and managing the national tobacco industry. The designed production capacity is 12,000 tons of cigarette paper and 6,000 tons of high permeability forming paper annually. Cigarette paper manufacturer, the company are committed to provide and support for the harmful subsidence reduction and carbon reduction of China's tobacco industry. (*Jnyawei.cn., 2018*)

The organic waste in this factory production wastewater can be treated by bacteria using aerobic, anaerobic, facultative and other bio/chemical treatment procedures. (*To, paper (1&2) 2020*) These type of biological/chemical digestive system can be utilised it in various production site such as biodiesel, paper production and various industrial level wastewater treatment facilities. The wastewater is the extraction from domestic use, animal husbandry, commercial activities, agricultural activities, surface runoff storm water and any sewer infiltration (*Qasim, et al 2017*). The biological growth in the wastewater causes different chemical reaction and production of various enzymes and its by-products, some of which are helpful for the industrial and commercial used. (*P. Melidis, et al 2009*). On the other hand, there are different physical filtration procedure and micronutrients balancing technique that can be used to change the removal rate or the chemical degradation for modifying the wastewater treatment rate, reduce the production cost and handling efficiency. (*J. E. Burgess et al 1999*) Anaerobic Digestion is a commonly used degradation process for wastewater treatment especially in the paper manufacturing industry where the presence of oxygen is not required (*Ozgun et al., 2013*). It helps to dissolves organic material using bacteria like hydrolysing, acidifying, methane producing and sulphate reducing species. The effectiveness of this project has been measured by the productivity and efficiency enhancement as the result of MNT combined with CWs technique which has compared to the conventional Anaerobic Digestion treatment method.

In this CTM case study, the Wastewater Treatment Plant (WWTP) is fifteen years old with 3000 M^3per day treatment capacity and the facility was designed for a 72 to 96 hours (*approx. 3 - 4 days*) hydraulic retention time which the facility is located at the southern part of China where warm climate by average ambient temperature of 20 degree C or above all year round. This helped the natural evaporation of some of the wastewater and advantage for the biologic treatment efficiency. *(China National Meteorological Information Centre - www.data.cma.cn)*

This WWTP is equipped with a physical filtration treatment module called Biological Aerated Filter (BAF)+ Ultra Filter (UF) and after it has two times Anaerobic plus Aerobic (A^2O) with activated sludge technique design. The treatment efficiency during 2017 to earlier 2018 were remaining between 60 - 75 % removal rate in its plant historic data indicated, that was before the MNT + CWs treatment modules added. To analysing the low treatment efficiency was related to a residual substance in wastewater called Polyvinyl Alcohol "PVA" - $(C_2H_4O)_x$, this is a water soluble substance from the product manufacturing process. Residual PVA has increased the WWTP operation cost and restricted the treatment efficiency. Based on our previous experiments in biodiesel WWTP in 2018, we have dosing the MNT with the intension of maximising the hydraulic retention time which is done at the upstream buffer tank and later after the MNT module built prior to the A_2O biological section of this WWTP. (*see Fig 1 and table 2*)

The CWs built were the intension of increasing the hydridic retention time for another 48plus hours(approx. two to three days) where the natural medias would act as the additional filters to the wastewater treatment from the factory. The construction of CTM's CWs was made relatively easier due to the factory site was located at the nearby village old water reserve facility. Hence the building up of the new CWs are only taken 1/3 of the normal cost of 3 x 3500 m^3 = 10,500 m^3 capacity conventional construction and able to complete the build-up in short space of 6 months' time. The identification of the effectiveness will also allow to implement these MNT techniques, so that the cost to current organic bio-digestive systems can be reduced with more productive alternatives. Currently a large amount of coagulants like Poly aluminium chloride (PAC) and Polyacrylamide (PAM) are used in this WWTP, it is always a cost saving opportunity for the alternative treatment method.

The combine implementation of MNT with CWs technique could reduce the consumption of PAC and PAM additive; as well reduction of noxious odour may lead to degradation of the metallic equipment used in this WWTP facility. In the following section the principles of the used of this technique will be discussed than followed by the method, result and analysis of this pilot study.

2. Material and Method

2.1 Procedures and Site Formation

Before the facility upgrade, CTM were used the Biologic Aerated Filter (BAF) + Ultra Filter (UF) combined with Anaerobic Digestion (A^2O) Technique in its WWTP. This study was conducted within the WWTP treatment plant without major construction works before the effluent discharging into a man-made lagoon or known as Constructed Wetlands (CWs). CWs will complete the final digestion and it acts as the natural filtration system before effluent discharge to the nearby local River instead of the local Community Wastewater handling facility. Therefore, the discharged effluent after CWs must meeting the China National & Industrial (*Paper Making*) by law discharge criteria.

2.1.1 Directional Trial - April 2018

Prior to the facility upgrade and the full-scale pilot study, a directional experiment conducted during March to April 2018. The reason being a residual chemical subsidence called PVA had often caused blockage at the BAF module. These blockages had significantly decreased the efficiency of the entire treatment plant and generated a limitation factor to the downstream biological A^2O treatment module.

In this pilot study a1000 ppm of MNT was dosed at the buffer tank which is at the equalization process for the WWTP (based on our previous projects in a similar size WWTP, the 1000ppm MNT dosage converted to0.375 L MNT per minute, hence 22.5 L per hour and 540 L per day.)

The dosage was based on one time shock dose of 748.8 L at the beginning of MNT treatment procedure following by continue dosage of 0.375 L per minute at the buffer tank. These procedure shad given the extensive anaerobic and facultative bacteria a similar natural nutrient to its habitats and largely enhancing the metabolism rate at the buffer tank. It could digest some of the PVA or break it down to small fragment for precipitation. Also, the purpose of this April experiment was researching after MNT addition whether the process is able to reduce the consumption of Coagulant Polymers i.e., PAM(+ or -ve charge)& PAC(+ve charge) dependence and hence achieving the operations cost reduction. Coagulant polymer will normally act as the adhesive to the pollutants and make it suck to the bottom and become sludge. It can help the reduce pollutants in the wastewater especially the top layer.

The 1000ppm dosage of MNT 22.5 L per hour had converted to 31KG per hour PAC and PAM reduction. The industrial practice is normally based on the following: - Every 1 ton of PAC dosage will add 0.01% (i.e., 1-3 ppm or 1KG -3KG) of PAM depending onsite measurement of COD, BOD5, TSS etc. It based on these data and adjust the coagulant dosage. Hence in this pilot study, it has based the following: - 1000 ppm MNT dosage substitute 1000 ppm of PAC + PAM dosage. (*P. Gebbie, Opers. Guild, UCQ - Qld 4-6 July 2006*)

PAC and PAM coagulant composites required a fine balance otherwise it will produce large amount of wet sludge (the water deposited in its sludges often over 80%). The sludge dewatering process and deposable cost of this type of industrial sludge are also no value addedly high.

The reduction of PAM+ PAC Coagulants Polymer was progressively reduced in two steps 50% at the time, after that by monitoring at the effluent COD,BOD5, TSS and sludge water deposited conditions at the collection tank prior entering the BAF (*Fig 3A,3B &3C*). The coagulants reduction of PAC & PAM was based on above mentioned steps within the first 5 days and also observation on-site day to day collected data at the A_2O module.

2.1.2 Full Scale MNT + CWs Treatment pilot study - Sept to Dec 2018

Later after the MNT module and CWs built completed in the month of August, we had taken another set of data between September to December in the year 2018. The MNT reactor module was built with similar MBBR (Moving bed biofilm reactor) principle where MNT dosage was planted at 1000 ppm per hour identical to other 3000 Tons per day system in our pasted similar project experience. (*To paper (2) 2020*).

To measure the microbial activity and metabolism rate we took five specific measurement namely pH factor, Temperature, COD, BOD_5 and TSS (*Fig1& table 3*) comparing with National and Industrial (*Paper Making*) Wastewater discharge standard.

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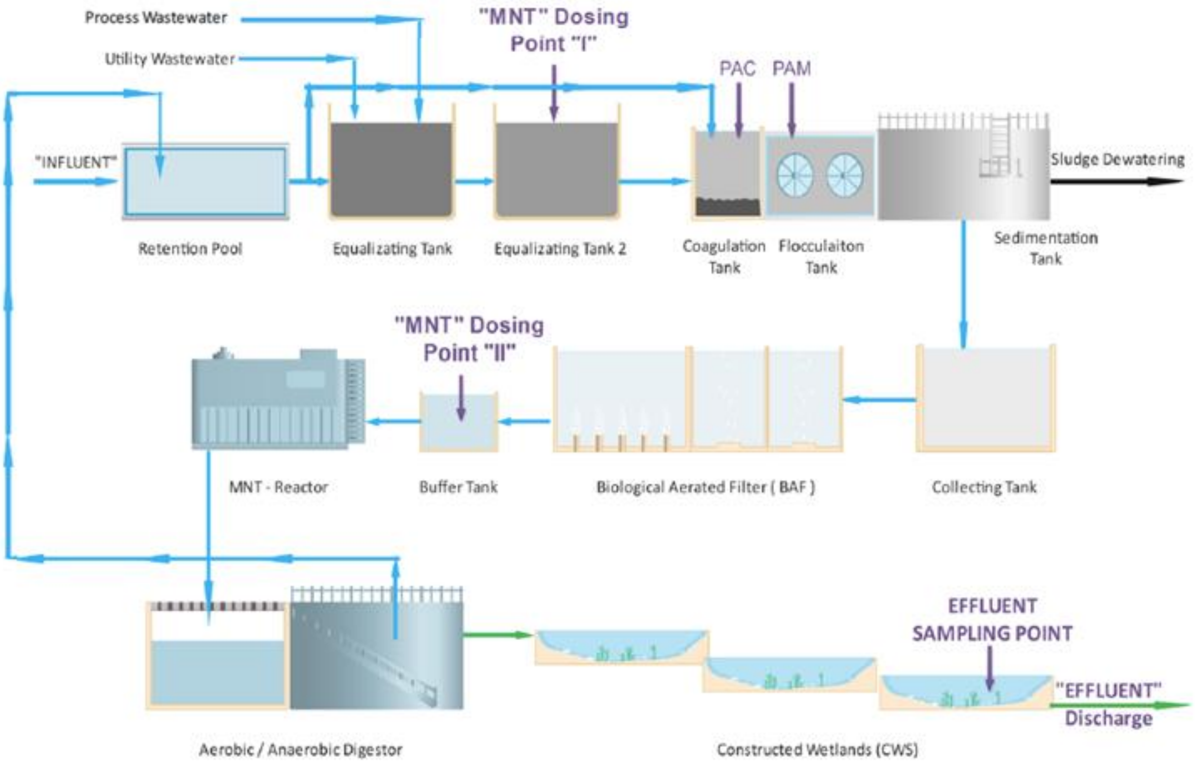

Figure 1: CTM renew WWTP General Layout with MNT dosing point & CWs

2.2 Micronutrient Technique (MNT)

Micronutrient is a process of adding organic nutrient like Vitamins and Mineral that enable anaerobic bacteria to break the specific organic compounds like sludge more effectively. (*J. E. Burgess et al 1999*) (*To, 1,2, 2020*). In this case study the MNT specific mix was including the four main elements; Amino acid composition, vitamin composition, purine and pyrimidine composition mineral composition.(*see Table 1*)

The anaerobic digestion procedure occurs without presence of oxygen where the hydrolysing,acidifying, methane producing and sulphate reducing bacteria are involved. The FOGis first broken into the VFA using Hydrolysing Bacteria. Using acidifying bacteria fatty acids is converted to Acetic Acid and the Aerobic bacteria covert this acid into new biosolids with water, carbon dioxide, methane (*Ge, Batstone & Keller, 2013*). In this process, the methane producing bacteria and sulphate reducing bacteria cause the generation of CO_2, H_2S and CH_4. MNT can reduce the generation of H_2S production while increasing the existing bacteria population microbial activity, reproduction and its metabolism rate (*Agu, Ibiene & Okpokwasili, et.al 2017*). The major advantage of this technique is that it can be used in any treatment plant irrespective of the influent and effluent amount. For 200 to 1000 ppm of MNT dosage, it can enhance the microbial activity of anaerobic/facultative bacteria and as a result the treatment efficiency can be increased. At the same time MNT can also enhance the settlement of suspended solids in wastewater with increased sedimentation, while increase the total sludge volume index (TSVI) for more productive input (*Zhou, Peng & Xiao, 2017*).
The Mix of MNT in this study is shown in the following "table 1".

Table 1: MNT mix ingredients

Components	Chemical formula	Percentage of Content (%)	
		Min	Max
Zinc sulphate heptahydrate	$ZnSO_4.7H_2O$	*3*	*4*
Manganese Sulphate Monohydrate	$MnSO_4.H_2O$	*2*	*3*
Globular (Water Soluble) Protein		*2.3*	*3.3*
Benzoic Acid	COH_5COOH	*0.2*	*0.5*
5 - hydroxymethylfurfural	$C_6H_6O_3$	*0.2*	*0.5*
hydroxy-butanedioic acid	$C_4H_6O_5$	*0.2*	*0.5*
Water	H_2O	*87.4*	*82.5*
total MNT ingredient %		*100*	*100*

2.3 Constructed Wetlands (CWs) - the natural filtration technique

CWs is a natural filtration technique are widely used likeSludge drying reed beds (SDRBs)technique that helped even many medieval civilizations to purify their water. In this case industrial wastewater treatment with this natural filtration can be used. The CWsnatural filtration technique has three continues zones and is a combined filtration using different materials such as Sand, Oysters Shell, Plants, Charcoal, Coconut fibres, Wood Chips, Pebbles and Gravel Stones etc... together with vegetation like reeds, water lily etc. where the plant roots can perforate the soil layer hence increase the oxidation process in the soil/sludge layer.

In this CWsnatural filtration technique different layers are used to filter the water from different level of TSS & TDS (*Fig 2*). Usually all these materials are stored in multiple beds as per a vertical model chamber (*P. Melidis et al 2009*). The water passes through the top to bottom layer using the gravitational force to maintain the flow. Pebbles bed is used to trap large material in wastewater that includes plastic materials, metallic structure, glass and others. At Zone 1, any material with diameter of more than 5 millimetres is trapped in this pebble bed. The bed of sand can filter smaller suspended particles. In Zone 2, sand particles as small as 25 ηm can be trapped in the sand bed (*Nzung'a, Kiplagat & Paul, 2020*). Charcoal bed is usually used in lower level of natural filtration chamber. In Zone 3, the carbon in charcoal helps to trap FOG to some extent and any particles larger than 1 ηm. Charcoal bed can act like an active carbon filter it can reduce thoselevel of heavy metals like *Cu, Cd, Ni, Pb, Zn, Cr Mn and Fe* etc. in the wastewater. Coconutbed is also used to filter this water because of its layers of fibre. Commercially, coconut carbon filter is used to trap chlorine particles, suspended matters, Volatile Organic Compounds (VOC), cryptosporidium and giardia and dissolved inorganic substance (*Ncube et al., 2018*). The Natural Filtration Technique (NFT) often used a combined or support filtration technique with other filtration techniques.

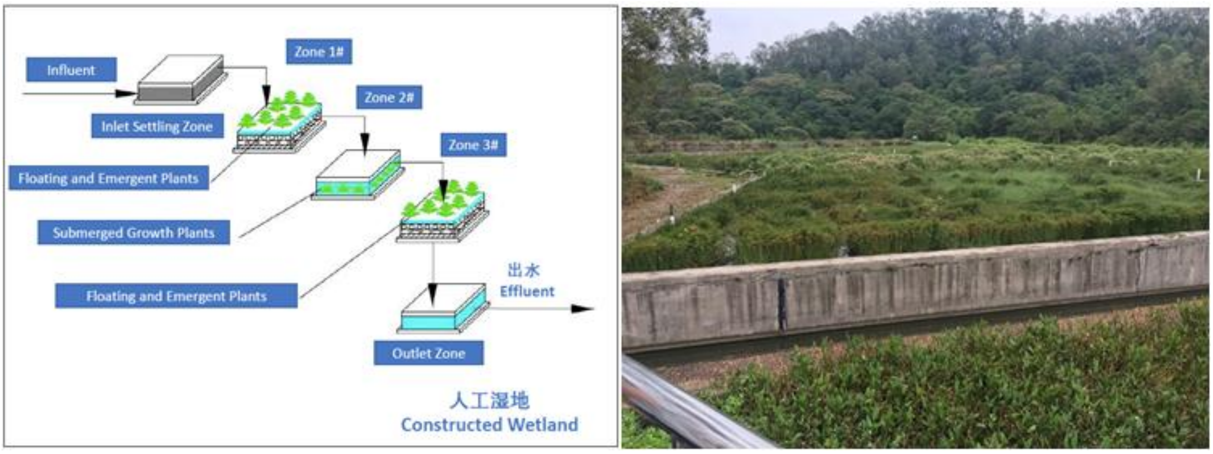

Figure 2: The CTM Construction Wetlands (CWs)

3. Results and Discussion

3.1 With and Without MNT

While the MNT module &CWs were under construction, a directional experiment conducted this is to see whether the WWTP efficient improve and the dependence of PAM and PAC able to reduce. It has found in general the biological reaction enhanced at the equalization stage. After dosing MNT at the Buffer Tank 2 and effluent sampling collected at the A_2O, found that the pH value is appeared a lot stable comparing to without MNT in March. The result of COD, BOD_5, TP, NH3-N and TSS has echoed our finding of some notifiable increase of removal rates. From the following presentation of effluent measurement (*table 2*), it can be found that the level of BOD_5 is reduced in both with and without MNT dosage. However, the peaks of with MNT dosage is significantly lower than that the peaks of without MNT dosage. It clearly shows that MNT dosage is more effective and enhancing the facultative action required less oxygen for the bio digestion.

While the 1000ppm MNT substituted the consumption of PAM and PAC are recorded after the collected data of removal rate of COD, TSS and Sludge water deposit observations. The reduction of polymer was 50 % at the time. The collective consumption of PAM was reduced by 64 % and the use of PAC51.84% was also reduced. After the trade off, that is still a significant cost saving opportunity for the CTM Wastewater Treatment operations by substituted the polymer consumption with MNT.

Although the COD and $BOD_5$and TN were still not meeting both China National and Industrial discharge standard. A good directional indicator shown the biologic activities had improved after the MNT dosing. (*Fig 3.1, 3.2, 3.3, 3.4, 3.5 & 3.6).*

Table 2: Average Influent and Effluent Data with MNT - April 2018

March to April with MNT pilot trial					
Test ITEMs (mg/L)	Average (*with 90# Data*)		Removal Rate	China Paper Industrial Discharge Standard - GB3544/-2008	China National Wastewater discharge Standard GB3838-2002) Cat. V
	Influent	Effluent			
TEMP	49.6	34.2	NIL		
PH	5.19	8.52	Passed	6-9	6-9
TSS	1745.09	28.89	98%	30	
COD	293.05	77.33	74%	50	30
BOD	135.09	66.48	51%	20	6
NH3N	1	1.08	-8%	5	1.5
TN	82.6	2.75	97%	12	1.5
TP	0.21	0.3	-43%	0.8	0.3

Figure 3.1: March & April experiment with / without MNT - Ph value at the WWTP

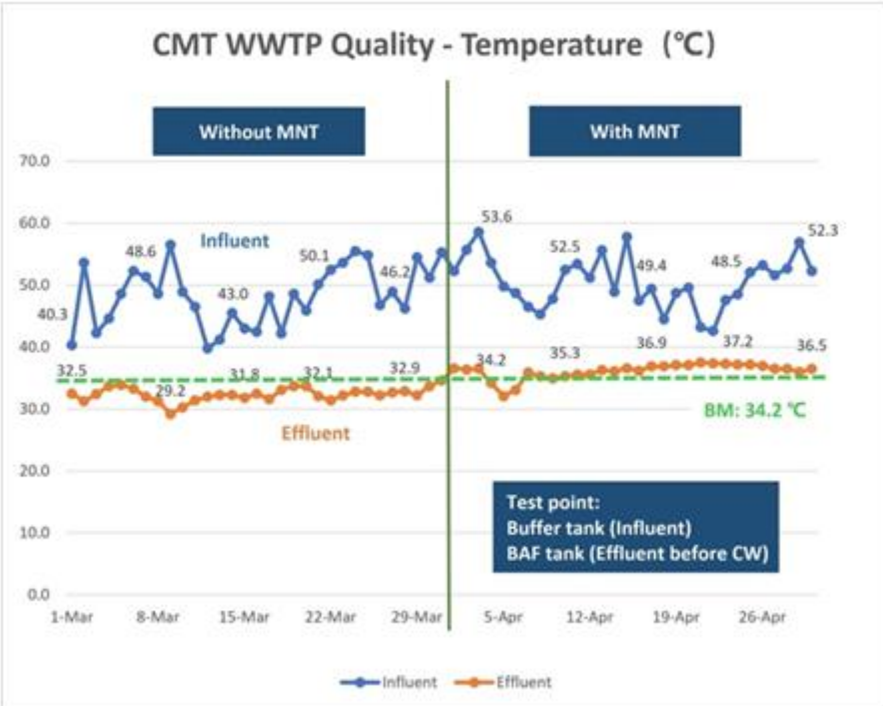

Figure 3.2: March & April experiment with / without MNT - Temp. at the WWTP

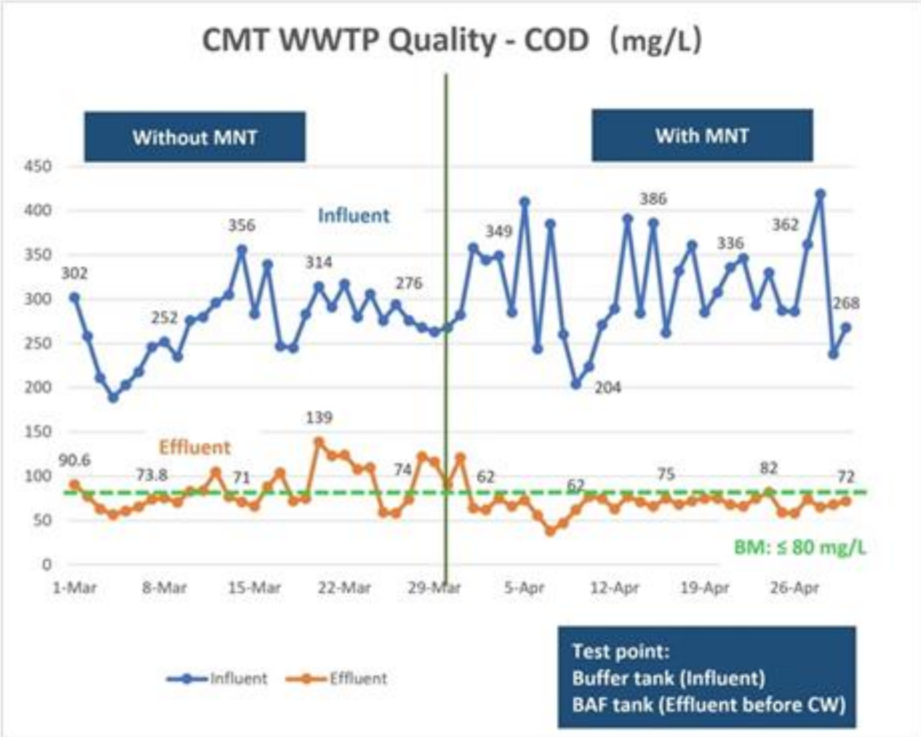

Figure 3.3: March & April experiment with /without MNT - COD at the WWTP

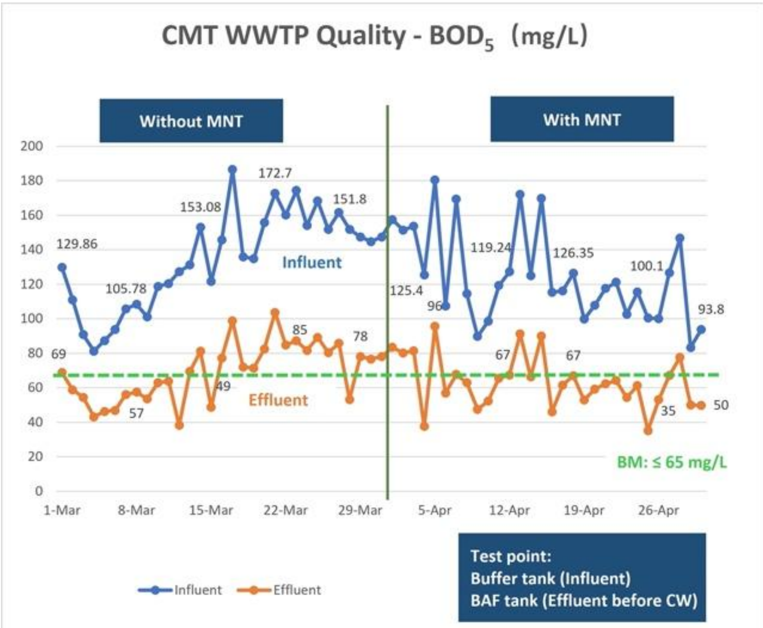

Figure 3.4: March & April experiment with /without MNT - BOD_5 at the WWTP

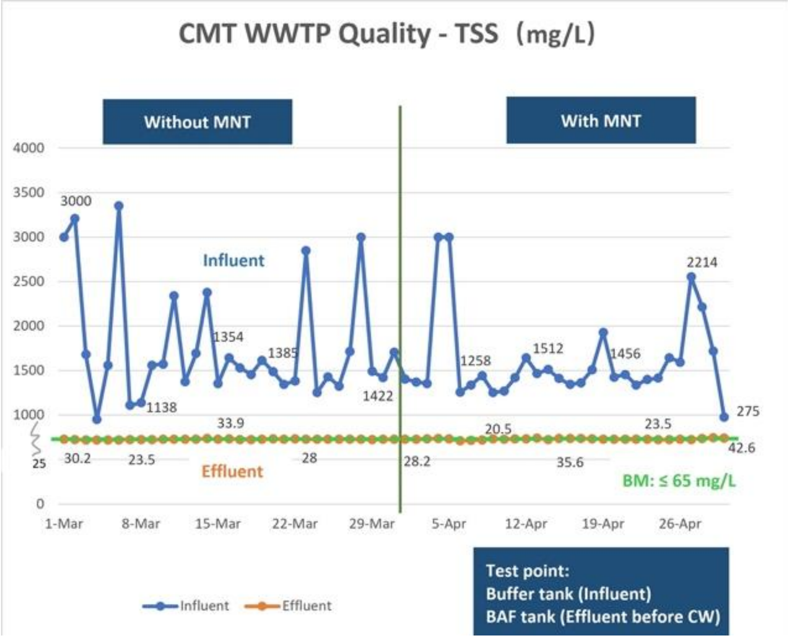

Figure 3.5: March & April experiment with /without MNT - TSS at the WWTP

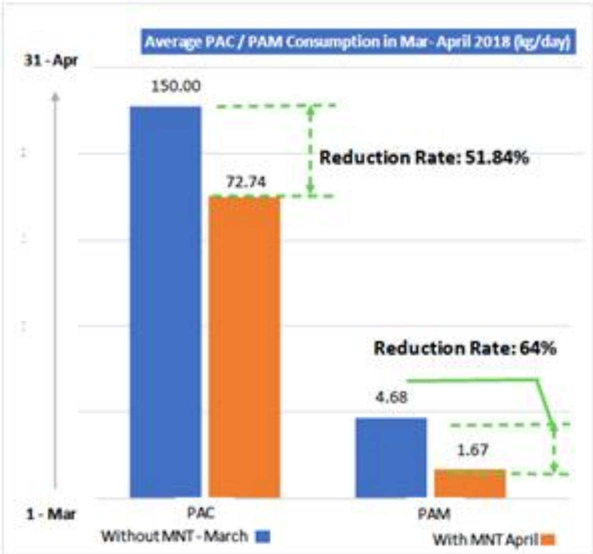

Figure 3.6: March & April experiment with /without MNT - PAM/PAC consumption

3.2 MNT combined with CWs Treatment

From September to December, another set of data were collected, it is by comparing the influent and efferent. With MNT module and CWs addition to the existing WWTP, it has increased the hydraulicretention time of36 to 48 hours (approx. 2 - 3 additional days). For the general wastewater treatment efficiency, it is an ideal situation.

The pH value shows very stable at7, this has provided a good biological condition for further facultative anoxic digestion in CWs. Temperature was in the region of 26 to 31 degree C where the hot weather has contributed the warmer condition in this wastewater treatment facility.

Three major indicators for WWTP efficient were also compared (*Fig. 4.1, 4.2, 4.3 & 4.4*). In this pilot study, COD average removal rate was 89% (*74% in April*), BOD_5 93% (*51% in April*) and TSS 97%(*98% in April)*respectively. The improve of COD, and BOD_5removal rate with MNT and CWs additional hydraulic retention time indicated an excellent improvement on biological reaction for the system. A comparison between 2017 and 2018 at the same period of time, indicated MNT dosing can caused significantly lower regular and exigent demand of coagulants application like PAC& PAM(*Fig5*). It has contributed the treatment efficient and significantly dropped in effluent flow. It indicates a significantly lower oxygen demand (like COD and BOD_5) and TSS suspended solids as a result of using MNT.

Some residual heavy metals were also tested on site, we found only small trace of it and found that the treated effluent was meeting the China National Discharged Criteria requirement. None of residual PVA found in the effluent in Sept-Dec data.

Table 3: Sept to Dec 2018 Average Discharge Data at WWTP with CWs

Sept to Dec with MNT + CWs					
Test ITEMs (mg/L)	Average (*with 175# Data*)		Removal Rate	China Paper Industrial Discharge Standard - GB3544/-2008	China National Wastewater discharge Standard GB3838-2002) Cat. V
	Influent	Effluent			
TEMP	49.6	34.2	NIL		
PH	5	7	Passed	6-9	6-9
TSS	1676.2	44.08	97%	30	
COD	316.46	35.24	89%	50	30
BOD	126.48	8.48	93%	20	6
NH3N	1.08	0.9	17%	5	1.5
TN	86.4	5	94%	12	1.5
TP	0.54	0.25	54%	0.8	0.3

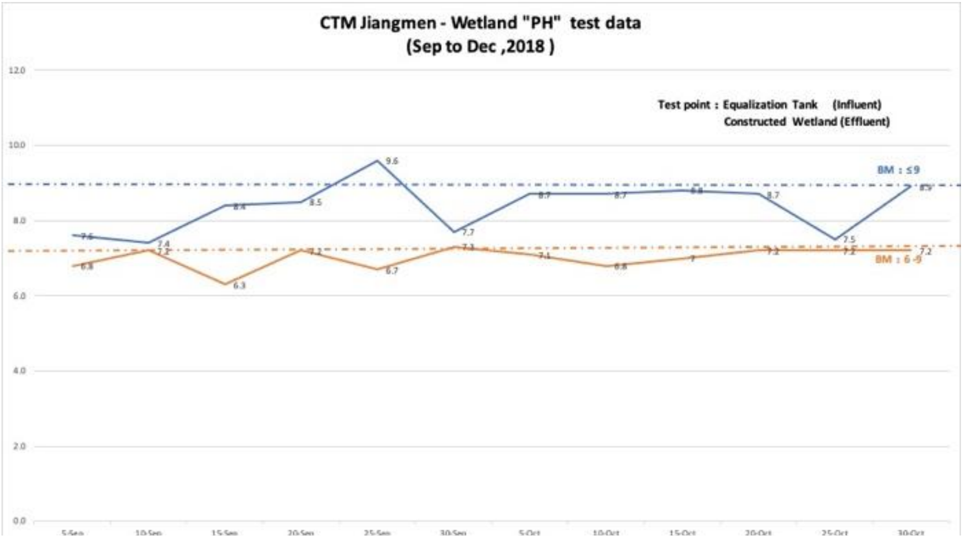

Figure 4.1: Sept to Dec - Ph Data after CWs commissioned + MNT

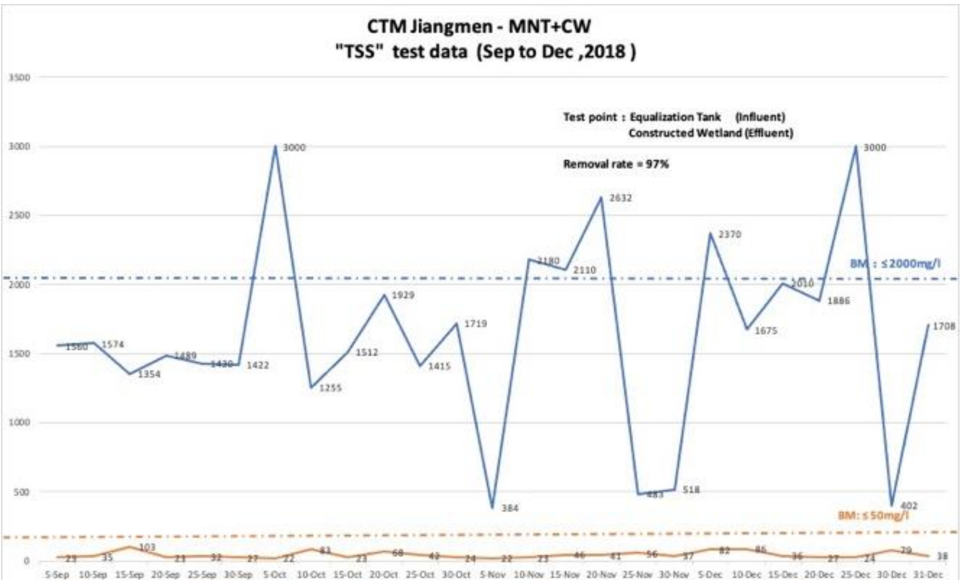

Figure 4.2: Sept to Dec - TSS Data after CWs commissioned + MNT

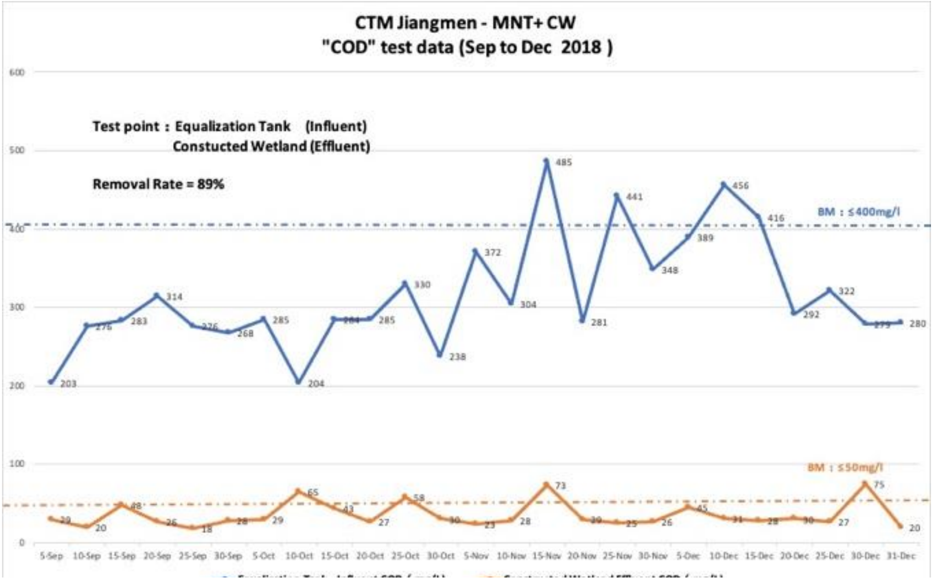

Figure 4.3: Sept to Dec - COD Data after CWs commissioned + MNT

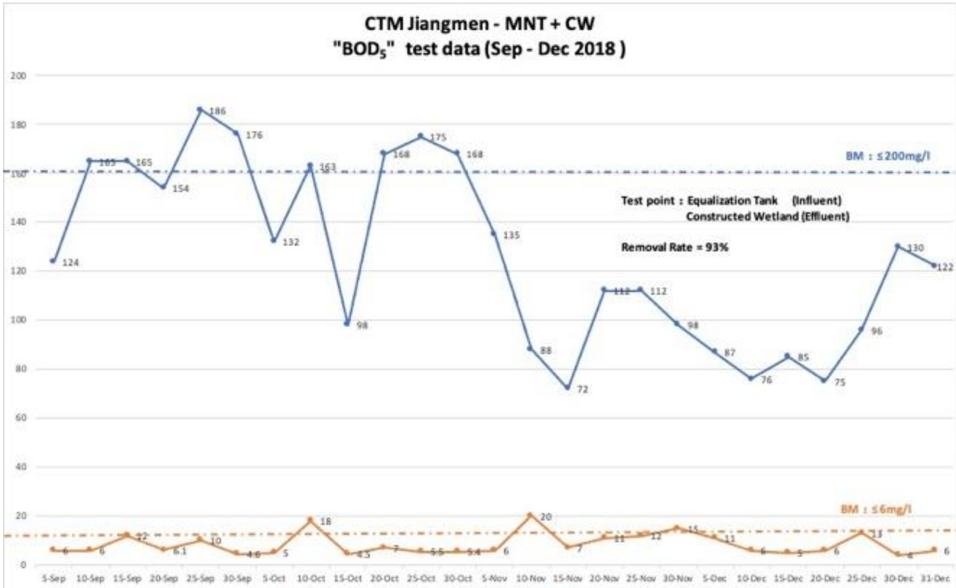

Figure 4.4: Sept to Dec - BOD5 Data after CWs commissioned + MNT

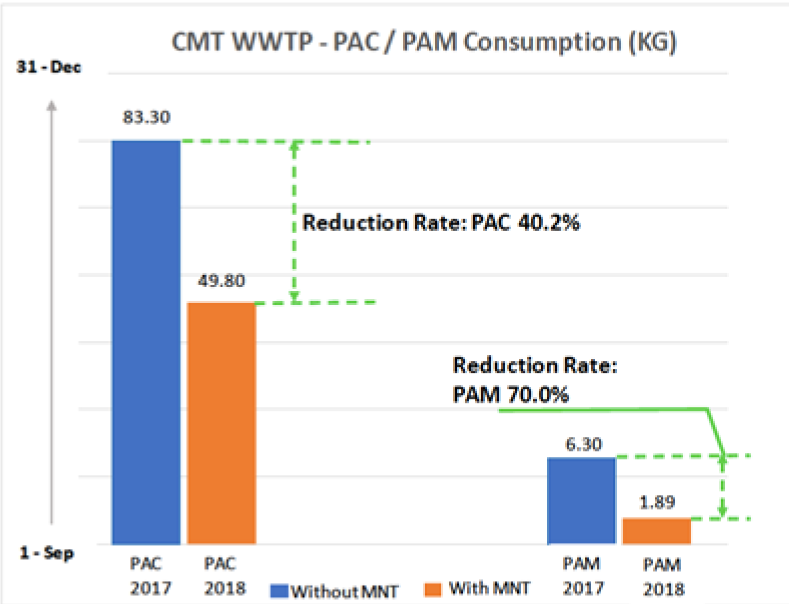

Figure 4.5: PAM & PAC Consumption 2017 vs. 2018

4. Conclusion

From both experiment and Pilot Plant study in China Tobacco Modi (Jiangmen) Paper Co., Ltd. (CTM) wastewater treatment system it can be interpreted that MNT have shown significantly more effectiveness in its WWTP production for the pollutants removal rate. Considering the TSS, COD and BOD_5removal rate, it can be said that MNT can highly reduce the level of oxygen demand. That increases the WWTP productivity and achieving the cost reduction by comparison to conventional approach. The lower level of TSS in both cases indicates that the BAF without blockage of PVA can be very efficient to remove suspend solids. The additional MNT process can be utilised to break down the suspended solid level at the earlier stage. The additional system with MNT and CWs treatment module were able to achieve very small sludge discharge. It is due to CWs had retained 90% plus residual sludges.

Other noticeable on-site condition was the odour issue, the application of coagulant like PAC and PAM that had induced some unexpected foul odour. This is due to saturation process at the settlement tank and caused more anaerobic digestion happening in this section of the system. With MNT presents, it has the facultative anoxic metabolic rate increased hence limited the reproduction of anaerobic bacteria doing the digestion instead.

The effectiveness of MNT for shows that it can enhance the biologic metabolism with the combined the treatment in CWs the natural filtration. It found the increase the metabolic rate while the COD and BOD_5 removal rate increased after passing through the CWs, also the retention time also helping the further treatment efficiency. One of the concerns are the residual metals in the effluent discharged, it is due to MNT ingredients during the biochemical digestion and releasing the element like Zn, Fe, Cu etc. In this case study, on site measurement of residual heavy metal and PVA are within the National Discharge Criteria allowable level where the CWs have retained most of the residual metals as well as the PVA.

One of the polluted subsidence PVA was not able to be quantified after the CWs. It is due to its water solubility property. Is MNT able to break down this subsidence or still it is still relied on Coagulant Polymer to have it lock down and transfer back for the system. This case study cannot claim any of the PVA removal as such. Having said that the discharged Effluent were improved and able to meet the bylaw standard after the MNT plus CWs treatment module installed.

Further consequents study opportunities present for the biochemical reaction when dosing over 1000 ppm of MNT for the PVA removal at this type of paper industrial WWTP.

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