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Performance Evaluation of Advanced Wastewater Treatment Technologies in Herbal Processing and Extraction Industry

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ABSTRACT

Due to enormous quantities with hazards and complexity in nature is a big challenge for effective treatment of wastewater from pharmaceutical processes including herbal extraction through conventional methods of distillation. The situation is further aggravated in countries facing high rising population, urbanization, and industrialization resulting in the generation of industrial wastes. The study has been carried out in the herbal extraction industry by conducting stage-wise sampling of ETP based on the conventional method and further coupled with ozonation as an advanced treatment to comply with regulatory standards. Additionally, the same process was studied that implementing the best available technology (BAT) by providing ETP with advanced technology modules such as MBR (membrane bioreactor) + RO + O₃ has not only resulted in compliance with standards but also reuse of treated wastewater into the process and utilities has been proved to be techno-economically a viable and sustainable option. Modifying existing aeration tanks and advanced oxidation through ozone injection post-biological treatment has resulted in COD and BOD reduction of 96.42% and 99.0% respectively. Whereas in the case of MBR + RO + O_{31} the values of pH, BOD, COD, TSS, and sulfide have been observed as 8.32, 2.0 mg.L⁻¹, 14.0 mg.L⁻¹, 1.0 mg.L⁻¹ and 0.0 mg.L⁻¹ respectively and 98% recovery of treated effluent, thus saving 44 KL.day⁻¹ of freshwater resulting into significant financial benefits of Rupees 12.59 lacs annually, which otherwise was outsourced through tankers.

INTRODUCTION

The most important food source for human beings is water only and every person has the highest level of consumption in his life cycle thus making its quality a very important issue. Thus, everyone should be concerned about the quality of surface as well as groundwater besides the adverse impacts of effluents entering into it. The removal effect of conventional pollutants such as POPs (Persistent Organic Pollutants has been in the limelight for the last decades and their behavior is well accustomed (Jones et al. 2005, Shahbeig et al. 2013). The wastes from herbal extraction and pharmaceutical processes contain drug residues with high chemical oxygen demand (COD) and Biological Oxygen Demand, pharmaceutically active compounds like hormones, antibodies (PhACs), and toxic organics. The pharmaceutical industries across the world indiscriminately generate huge quantities of residual pharmaceutical ingredients at the outlet of conventional wastewater treatment facilities (Parimal & Ritwik 2013). A big problem frequently encountered in handling wastewater from the conventional methods of herbal extraction and pharmaceutical processes is highly variable due to variations like the composition of raw material widely varying from one class of products to another, many pharmaceutical companies use the pretense of confidentiality of composition to escape from regulations of stringent pollution control norms (Parimal & Ritwik 2013).

Incomplete assessment of the magnitude and nature of toxic substances, the process wastes continue to be released into the environment. The irrelevant empirical relations of pharmaceutical ingredients, wastewater characteristics (COD, BOD, TSS, TP, and oil), operational parameters of flow, hydraulic retention time (HRT), and biodegradability index (BOD: COD) (Santos et al. 2009) makes the treatment process further complicated. Though a very high removal rate (80-100 %) is indicated for pharmaceutical products like ibuprofen, ketoprofen, and mefenamic acid, etc. a sludge retention time of around 10-20 days (Jones et al. 2005) is required. The detection of traces of pharmaceutical and personal care products in the discharges after CETPs (Common Effluent Treatment Plants) indicates the presence of persistent compounds organic and inorganic (Hedgespeth et al. 2012).

The other serious issue in the management of toxic wastewater from different industrial processes is mixing with sewage and further transferring to common effluent treatment plants resulting in very complex wastewater difficult to treat effectively. The recovery of these components from the waste waters is economically unfeasible. Under this distracting situation, evaluating the existing treatment technologies, and effective handling of toxic wastewater is necessary to come out with clear solutions for the implementation of advanced and sustainable technologies. The activated sludge can be compared with other similar processes making use of existing structures and equipment where final effluent quality can be improved in case it is subjected to tertiary treatment such as activated carbon adsorption, residual nutrients removal, etc. The overall reduction of selected pharmaceuticals like 68% of tetracycline, 78% for chloro-tetracycline and 68% of doxycycline (Karthikeyan & Meyer 2006, Yang et al. 2005) have been reported, however, the effectiveness gets weaker due to presence of pharmaceuticals active hormones, antibiotics as a residual component in the wastewaters. Now the research studies have established that Advanced Oxidation Processes (AOP) such as Fenton's treatment, ozonation, and Ultra Violet (UV) radiations, and their recombination can be very effective in the treatment of persistent pollutants generated from herbal extraction processes (Tong et al. 2011, Gupta et al. 2009, Sharma et al. 2013).

These (AOPs)s can be further coupled with the existing conventional activated sludge processes to meet regulatory requirements due to the enforcement of stricter discharge standards besides compliance with the orders of the Hon'ble courts. However, such measures without any resources add to treatment costs. So, the best option in the current situation is implementing a combination of advanced treatment and oxidation processes shall be effective for the removal of toxic residues in the final discharge besides resource recovery through the reuse of treated effluent into the process thus making the treatment sustainable in case these processes are further aided with ultra-filtration. The MBR-Ozone process can achieve the removal of antibiotic acetaminophen up to 98.4%. (Shabbeig et al. 2016)

MATERIALS AND METHODS

Background

The existing Effluent Treatment Plant of the unit manufacturing Colchicine (1200 kg per year) and Thiocolchicoside (1200 kg

Table 1: Effluent characteristics prior to modification.

Sl. No.	Parameters	Average Values in mg.L ⁻¹ except pH	Prescribed limits
1.	pН	6.23	5.5-9.0
2.	TSS	73	100
3.	BOD	240	30
4.	COD	420	250
5.	Sulfide	1.6	2.0

per year) was selected for the study. The unit was not able to comply with discharge standards due to the complex type of toxic chemicals being used in the process. The capacity of the old and new ETP is 30 KLD and 100 KLD respectively comprising physical chemical and biological treatment followed by tertiary treatment. There were numerous public complaints of old ETP regarding the discharge of effluent with inadequate treatment. The unit was under the surveillance radar of regulatory agencies. The treated effluent is being discharged into nearby Nalla having average values of BOD and COD exceeding the discharge standards prescribed as shown in Table 1.

Accordingly, the unit modified the ETP by replacing the existing perforated pipe with a type diffuser to produce fine bubbles which have further resulted in sufficient oxygenation in the aeration tank along with injection of ozone post-biological treatment. The flow chart of the ETP (Old) is as below.

The performance evaluation of different treatment units was carried out by conducting the stage-wise sampling of the effluent treatment plant. The reduction in values of other parameters after primary treatment has been observed for BOD and COD. The values of TSS have been increased in the aeration tank showing proper growth of MLSS and effective mass oxygen transfer after the replacement of the coarse bubble pipe diffuser with dome type. It has also been observed that the percentage of COD and BOD reduction after biological treatment has been observed as 96.42% and 99.48% respectively. Percentage reduction of sulfide values has been observed as 53.93% indicating low removal rates of sulfide. However, after injection of ozone post-biological treatment, a higher reduction in the values of sulfide levels has been observed with percentage removal reported as 67.66% and complying with discharge standards. The overall reduction in the values has been shown in Table 2 from where it can be inferred that there has been a reduction in all the



PCL- Primary Clarifier, AT- Aeration Tank, SCL- Secondary Clarifier, OT- Ozonation Tank, ACF- Activated Carbon Filter, SF- Sand Filter

Parameters	Collection Tank	After Primary Treatment	After Secondary Treatment System (Biological)	Final Outlet after Tertiary treatment
TSS (mg.L ⁻¹)	430	186	58	58
% Reduction		56.74	68.81	0
COD (mg.L ⁻¹)	5930	4453	159.33	181
%Reduction		24.90	96.42	0
BOD (mg.L ⁻¹)	4080	2541	13	12.5
% Reduction		37.72	99.48	3.84
Sulfide (mg.L ⁻¹)	10.33	9.4	4.33	1.4
% Reduction		9.00	53.93	67.66

Table 2: Stage-wise reduction (%).

parameters due to the replacement of coarse bubble diffuser with dome type besides injection of ozone post-biological treatment. The results regarding stage-wise reduction have been shown graphically in Fig.1 to 4.

Before modification of the ETP based on conventional treatment, the unit was not complying with the discharge standards and keeping in view the stage-wise sampling conducted to evaluate performance after the existing



Fig. 1: Stage-wise BOD reduction.



Fig. 2: Stage-wise COD reduction.

conventional ASP treatment was modified by increasing mass oxygen transfer and injection of ozone after secondary treatment has resulted into regulatory compliance. It has also been observed that values of sulfide have been reduced



Fig. 3: Stage-wise COD Reduction.



Fig. 4: Stage-wise Sulfide Reduction.

Sr. No.	Parameters	Pre-modification	Post-Modification	Prescribed limits
1.	pН	6.23	7.56	5.5-9.0
2.	TSS (mg.L ⁻¹)	73	58	100
3.	BOD (mg.L ⁻¹)	240	12.5	30
4.	COD (mg.L ⁻¹)	420	181	250
5.	Sulfide (mg.L ⁻¹)	1.6	1.4	2.0

Table 3: Comparative values of results at the final outlet of ETP.



Fig. 5: Pollution load reduction post-modification.



Fig. 6: Water balance after enhancement in production capacity.

considerably after ozone treatment. The analysis results of various parameters pre and post-final out have been shown in Table 3 and graphically represented in Fig. 5. The results

shown in Table 3 indicate that post modification the unit is complying with discharge norms; however, it is pertinent to mention that there was no reuse of treated effluent. In the

Treatment Stage	Parameters							
	TSS	Removal %	COD (mg.L ⁻¹)	Removal %	BOD (mg.L ⁻¹)	Removal %	$O\&G (mg.L^{-1})$	Removal %
Collection Tank	980		10500		3500		16	
Anaerobic (1 st Stage)	294	70	5250	50	1225	65	9.6	40
Anaerobic (2nd Stage)	71	76	1857	65	306	67	4.3	55
Aeration + MBR	7	90	275	85	16	95	3	30
RO Outlet + Ozone	1	98	14	95	2	95	0	100

Table 4: Stage-wise results post implementation of MBR and Advance Technologies.

meantime, due to increased market demand for products, the unit was in process for further enhancement in the production capacities where the effluent load besides water consumption from the process shall be increased.

The water balance according to enhanced capacity is shown in the Fig. 6.

Keeping in view experience and targeting stricter environmental norms a new ETP of capacity 110 KLD was installed by replacing the old one. However, the management was indecisive about the selection of proper treatment technologies. Accordingly, the management took the decision and implemented a proposal based on advanced technology such as two-stage anaerobic treatment, MBR (Membrane Bio Reactor) further coupled with Ozone and RO treatment to meet ZLD (Zero Liquid Discharge) requirements, keeping in view the following advantages are being foreseen in the new ETP with MBR as main module being implemented by the unit as below.

a) Due to the use of a membrane bioreactor, the



Fig. 7: Stage-wise reduction of TSS.

life RO membrane is increased from 4 months to about 8 months. In addition to this, there is considerable saving on account of water cost being outsourced.

1651

- b) By implementation of MBR coupled with an RO filtration system, the area requirement shall be on the lesser side in comparison to MBBR. ETP with MBR module shall occupy 30% less space.
- c) The treated effluent can be reused in the process besides toilet flushing and on land irrigation resulting in the conservation of natural sources besides the removal of inert organics. Without MBR+RO+O₃, 50KL of fresh water was being outsourced through tankers costing around Rs. 50/KL (incl. cost of water + transportation). Post implementation of these advanced technologies with the MBR module 85-90% of daily freshwater consumption has been reduced thus saving around Rs. 10-12 lakhs annually
- d) The lower power consumption in the case of MBR shall result in savings of around Rs. 2 Lakhs annually in comparison to MBBR.



Fig. 8: Percentage of TSS removal stage-wise.



Fig. 9: Stage-wise reduction of COD.



Fig. 10: Percentage COD removal stage-wise.

The stage-wise reduction of parameters such as BOD, COD, TSS, and Oil and Grease have been shown in Table 4 and graphically is represented in Figs. 7 to 12.

It can be inferred from Table 4 and Figs. 7 to 12 that maximum COD removal efficiencies have been observed as 85% and 95% for aeration + MBR + O_3

Table 5: Comparative values of results at the final outlet of E	TP.
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Fig. 11: Stage-wise reduction of BOD.



Fig. 12: Percentage BOD removal stage-wise.

and RO outlet whereas BOD removal efficiencies have been observed as 95% in both situations and the treated wastewater is reused in the process. Due to the use of a membrane bioreactor the life RO membrane is increased.

The comparative values of various parameters post modifications in the conventional treatment system and the combination of MBR + RO + Ozone are shown in Table 5 and represented graphically in Figs. 13.

Sl. No.	Parameter	Post-Modification (Conventional + Ozone)	MBR+RO+O ₃	Prescribed limits
1.	pH	7.56	8.32	7.50
2.	TSS (mg.L ⁻¹)	58	1.0	100
3.	BOD (mg.L ⁻¹)	12.5	2	30
4.	COD (mg.L ⁻¹)	181	14	250
5.	Sulfide (mg.L ⁻¹)	1.4	0.0	2.0



Fig. 13: Final outlet values post-modification.

CONCLUSION AND RECOMMENDATIONS

The overall reduction of 99.48% in the case of BOD, 96.42% in the case of COD, 68.81% in the case of TSS, and 53.93% has been reported due to an increase in mass oxygen transfer after the replacement of coarse bubble diffuser with fine bubble besides injection of ozone post-biological treatment based on a conventional system. It has been further established that a combination of advanced treatment (MBR) coupled with ozone has resulted in further improvement in the overall treatment by reduction of BOD, COD, TSS, and Sulfide by 99.8%, 99.0%, 93.75%, and 94.80% respectively and shall result into 98% recovery of treated effluent and saving 44 KLD of fresh water and financial benefits of Rs. 12.59 Lakhs annually besides reusing treated wastewater for toilet flushing, irrigation as resource recovery option. In addition to this, the area requirement for secondary clarification is almost negligible. Therefore, the use of advanced treatment technologies comprised of membrane bioreactor further coupled with RO and ozonation is recommended for complex organic wastes generated from herbal extraction and bulk drug manufacturing industries. The management of RO reject is an issue in this situation due to high TDS, accordingly subjecting the same to MVR (Mechanical Vapor Recompression) System can also be recommended.

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