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Wastewater Nutrient Changes Lead to Savings for Mill Owners

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As pulp and paper mills strive to survive in increasingly difficult economic times, many mills attempt to improve and expand their production processes. Consequently this generates larger volumes of contaminated wastewater and increased use of chemicals to deal with that contamination. Without serious thought and planning given to management of wastewater treatment processes, those processes can easily become unbalanced or insufficient to meet the increased demand placed on them.

In this article, we discuss the significance of wastewater bioremediation and the important roles played by microorganisms and the structured nutrition systems required to effectively manage the biological ecosystems necessary for effective and cost-efficient wastewater treatment. We also describe three internal case studies conducted at pulp and paper mills to demonstrate the effectiveness of different approaches to nutrient management in wastewater bioremediation.

The Pulp and Paper Industry

The pulp and paper-making industry is very water-intensive and ranks third in the world in terms of freshwater withdrawal (as much as 60 m^3 of water per ton of paper produced).[1] The untreated mill wastewater, being rich in recalcitrant compounds, can potentially be very polluting: over 250 chemicals have been found in mill effluent, including harmful components such as resin acids and sterols.[2]

Pulp and paper mill wastewater is typically treated with mechanical technologies, followed by biological and/or chemical methods. Discharge standards are defined based on characteristics such as biochemical oxygen demand (BOD—the amount of dissolved oxygen needed by aerobic biological organisms to break down organic material in water), chemical oxygen demand (COD—indirectly measures the amount of organic material in water), total suspended solids (TSS), total nitrogen, and total phosphorus. Other tested indicators can include average mixed liquor suspended solids (MLSS—the concentration of suspended solids in the aeration tank during the activated sludge process), and average SV30 (a measure of sludge settleability).

Bioremediation

Bioremediation is the process of engineering environmental conditions to encourage the growth of certain naturally occurring microorganisms (such as bacteria, fungi, algae, and enzymes) that use contaminants as a food source. Under the right conditions microorganisms consume and digest contaminants, usually converting them to small amounts of water and harmless gasses such as carbon dioxide and methane (process dependent).

Compared with other approaches, bioremediation processes for wastewater treatment are considered to be of cost benefit, eco-friendly, and suitable for reducing BOD and COD from the wastewater.[3] The most commonly adopted pulp and paper mill biological treatment methods are activated sludge process, anaerobic lagoon, stabilization pond, and their modifications.[4]

Wastewater Microorganisms and Nutrition

Microorganisms are found everywhere on earth under every condition imaginable, and pulp and paper mill wastewater is no exception. For microorganisms to be fully effective in their bioremediation role, it is essential that mill operators create a stable ecosystem for them and closely monitor it. Key to that ecosystem is the provision of needed macronutrients (nitrogen, phosphorus, sulfur, potassium, etc.) and micronutrients (zinc, manganese, molybdenum, etc.)—as well as a carbon source in order for microorganisms to survive, replicate, and consume and treat wastes.[5] Each vitamin and mineral is essential to microorganism growth and metabolism and has a unique and specific function to perform. Most wastewater treatment systems rely solely on their primary influent to provide food and nutrient sources to their microbial systems: this can result in key nutrient deficits resulting in wastewater system imbalances or deficiencies.

The consequence of neglecting these imbalances can be significant. Signs of nutrient deficiency include sludge bulking, foaming, poor settleability, inefficient removal of suspended solids, odor, excess sludge, and inefficient removal of BOD or COD. For example, many foaming and sludge-bulking issues are due to excessive filamentous bacteria that thrive in nutrient-deficient environments and prevent settling. It is important to understand that providing bioavailable nutrients can improve the process while reducing the overall volume of chemicals required. This facilitates the growth of healthy microorganisms, which in turn leads to more stable and efficient wastewater treatment processes.

More stable processes also allow for desirable higher microbial life form development, such as amoebas, ciliates, rotifers, etc. These higher life forms are necessary for efficient wastewater treatment, as they feed mainly on loose bacterial cells. Lack of these higher life forms leads to sludge build-up and can also be indicators of toxicity or the lack of available nutrients in wastewater systems, which lead to inefficient and more costly mill operations.

Case Studies: 3 Pulp & Paper Mills

In this section, we provide the results of three case studies that discuss the use of one specific Probiotic Solutions® liquid product utilized in the bioremediation processes of three pulp and paper mills in China. The product involved is Super Phos® (SP), a tech-grade white phosphoric acid and monoammonium phosphate source that is pre-complexed with Micro Carbon Technology® (MCT®), a proprietary process that converts a soft, humic material into extremely small oxygen-rich carbon molecules. The MCT® process results in a carbon source that is an ultra-efficient vehicle/carrier—due to the micro-carbon molecule's low molecular weight, greater specific surface area, and higher cation exchange capacity—to deliver readily bioavailable nutrients to microorganisms.

Mill #1

Mill #1 treats 30,000 m^3/day of wastewater. It traditionally used 85% industrial-grade phosphoric acid as a phosphorus source in its activated-sludge wastewater treatment system. Bench tests were conducted to evaluate if smaller amounts of SP could replace the mill's current phosphorus source. The test utilized five-liter reaction vessels, with the source wastewater being 3.58 liters from the first clarifier inlet and 1.42 liters of returned activated sludge (RAS). Dissolved oxygen (DO) levels of 2mg/L were maintained in the vessels using small aeration pumps. Each test lasted 5 days, with two grab- samples collected daily and averaged. Each sample was analyzed for COD, DO, and Total Phosphorus—per industry standard protocols. Two tests were developed: the first used SP to replace the phosphoric acid source with a 1 to 4 ratio, while the second used SP to replace the phosphoric acid source with a ratio of 1 to 5. The control ran in parallel, using the existing phosphorus source.

The first clarifier inlet COD was then compared with the control COD effluent as well as the two test results. It was found that at both ratios of SP, COD levels were comparable to the control (see Table 1). Total phosphorus levels were also compared with the first clarifier's inlet, the control, and the two tests, as well as to the governmental standard of 0.50 mg/L (see Table 2). While it was found that the first test, with a SP ratio of 1 to 4, had a slightly higher value than the value from the inlet to the first clarifier, it was still under the required standard for Total Phosphorus. The second test, with a ratio of 1 to 5 of SP, came in under the value of the first clarifier.

Table 1. Mill #1, Comparison of 1st Clarifier Inlet COD to Average Effluent COD per Day of Testing

Test Day	1st Clarifier Influent COD (mg/L)	85%Phos Acid COD (mg/L)	SP (1:4) COD (mg/L)	SP (1:5) COD (mg/L)
1	505	52	58	No Test
2	536	50	47	No Test
3	511	54	44	45
4	622	36	38	36
5	640	23	29	26
6	605	68	No Test	64
7	639	63	No Test	65
Range	505-640	23-68	29-58	26-65

Table 2. Mill #1, Testing of Total Phosphorous in Effluent

Test Day	1st Clarifier Inlet Total P (mg/L)	85%Phos Acid Total P (mg/L)	SP (1:4) Total P (mg/L)	SP (1:5) Total P (mg/L)
1	0.27	0.37	0.46	No Test
2	0.29	0.31	0.27	No Test
3	0.24	0.22	0.17	0.26
4	0.26	0.19	0.14	0.23
5	0.32	0.16	0.1	0.12
6	0.29	0.14	No Test	0.12
7	0.31	0.15	No Test	0.11
Range	0.24-0.32	0.14-0.37	0.10-0.46	0.11-0.26

Table 3. Mill #2, COD Removal Rate for SBR Tank 3 and SBR Tank 4

Index	SBR Tank 3	SBR Tank 4
Phosphorous Source	Super Phos®	Typical Phos. Acid
COD Removal Rate	84%	81%
Avg. MLSS	1941 mg/L	1949 mg/L
Avg. SV30	72	73

Grab-samples of the control as well as the two tests were also collected and viewed under 100x magnification; in all three samples, higher life forms were found (rotifers, stalked and free-swimming ciliates), indicating a healthy microbial population with no visual changes among the three samples.

Mill #2

Mill #2 has the capacity to produce 1,800,000 metric tons of pulp and 3,100,000 metric tons of paper a year. Its wastewater system consists of four parallel sequencing batch reactors (SBRs), followed by an aeration system that treats 50,000 m^3/day and meets all national and local province standards.

For this test, Tank 3 and Tank 4 were selected, while Tank 1 and Tank 2 were maintained under normal operations. Tank 3 was used to test the replacement of the typical liquid phosphoric acid with SP, and Tank 4 was set up as the control. Testing occurred over 7 days. For this test, SP incrementally replaced the typical phosphoric acid over the course of three days to a final reduced ratio of 1 to 4 to minimize any potential impacts (system upsets, over-dosing, etc.) to Tank 3.

The COD removal rates were monitored for both tanks during the test. In addition to COD removal, average MLSS and SV30 were tabulated for further evaluation of the SP efficacy. It was found that both tanks were statistically equivalent in all three metrics, with Tank 3 having a COD removal rate that was 3 percentage points better (see Table 3).

Mill #3

Mill #3's existing wastewater treatment system uses 600 kg/day of diammonium phosphate (DAP) as a phosphorus source to maintain a healthy microbial population for wastewater treatment. The facility's effluent has a COD of 200 mg/L. The plant's goal was to continue to reduce costs while maintaining the same efficiency.

The facility replaced 600 kg per day of DAP with a much lower daily dose of 75 kg SP. This large reduction in chemicals reduced the amount of storage space required as well as labor costs involved in moving and dosing the product. In addition, by using SP the chemical costs were reduced by over 17%. Treatment efficiency was maintained as well, as the effluent COD remained at 200 mg/L. Furthermore, afterward the sludge microbiology was more active with more vigorous regrowth.

Conclusions

Wastewater treatment is an area that often garners less attention from mill owners than other operational areas. By maintaining a healthy microbial population within the biological portion of the wastewater treatment system, the treatment facility can ensure that it is operating at peak performance.

Bioavailable phosphorus is absolutely necessary to develop and maintain a healthy microbial population in the wastewater treatment system. Utilizing a bioavailable phosphorus source such as Super Phos® with Micro Carbon Technology® improves system performance while greatly reducing the volume of phosphorus required and the resulting phosphorus levels in the effluent. This leads to cost savings that all mill owners are looking for while maintaining the treatment system's operational effectiveness.

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