PEER REVIEWED

Effect of paper machine additives on the health of activated sludge

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ABSTRACT

This study examines batch respirometry as a screening tool to identify problematic papermaking additives that could disrupt the biological treatment of mill effluent. The method rapidly evaluates the toxicity of paper additives by tracking oxygen consumption of the respiring microorganisms in the activated sludge. Batch screening tests of 20 paper additives indicated that three paper dyes, a cleaner/solvent, and a microbiocide were the most toxic to the respiring biomass, while polymeric additives had no significant impact. A four-month pilot study with an orange dye confirmed the validity of the rapid respirometric method coupled with microscopic examination. The results also show that biological treatment systems can recover from the impact of harmful additives.

Application:

Demonstrates the utility of batch respirometry, a rapid method of screening papermaking additives for potentially harmful effects on activated-sludge treatment systems.

BIOLOGICAL TREATMENT SYSTEMS are widely used as secondary treatments to purify pulp and paper mill wastewater. Many mills rely on the activated-sludge process, and a major upset in this treatment system could result in noncompliance with government regulations, requiring a complete or partial shutdown of the mill. Clearly, mills have a strong incentive to understand how pulping and papermaking processes can affect the performance and stability of their effluent treatment systems.

The manufacture of specialty-grade paper from a mechanical pulp furnish requires the use of several chemical additives. Typical paper additives include azo dyes, modified starches, inorganic minerals, and synthetic polymers. These chemicals affect paper properties such as color, strength, density, and surface properties. However, the potential downstream impact of paper additives on a biological treatment system is not clear. One way to assess the impact on a biological system is to measure the effects of these chemicals on the oxygen uptake rate (OUR), offline, using a respirometer.

The research presented here had two principal objectives:

1. Identify potentially problematic chemicals through a screening process utilizing respirometry
2. Operate a pilot plant to test the application of respirometry as a screening tool while investigating the long-term effects and physical manifestations of papermaking chemicals.

This research was carried out at Abitibi-Consolidated's Iroquois Falls mill using whole-mill effluent and biomass from the activated-sludge (secondary) effluent treatment plant. The mill's aerobic activated-sludge system contains an aeration basin with a hydraulic retention time of 24–30 hours. The system consistently achieves BOD (biochemical oxygen demand) removal exceeding 95%, and the effluent is 100% nontoxic.

BACKGROUND

Respirometry is a technique for continuously measuring the oxygen uptake of microorganisms. Many other techniques have also been developed to monitor biomass activity, including measurement of dehydrogenase activity using triphenyl tetrazolium chloride (TTC), measurement of reductant activity, and measuring the concentration of adenosine triphosphate (ATP) *(1, 2)*. Respirometry was chosen in this study because it provides a fast, reliable indication of microorganism activity that is directly related to the consumption of BOD.

Equation 1 illustrates how a respiring biomass oxidizes and assimilates a simple carbon source (e.g., a carbohydrate CH_2O):

$$\text{Biomass} + \text{Nutrients} + CH_2O + O_2 \rightarrow CO_2 + H_2O + \text{Energy} + \text{Biomass} \quad (1)$$

In a closed reactor system containing actively respiring biomass, the pressure in the headspace would remain approximately constant, since CO_2 production is approximately balanced by O_2 consumption. The precise ratio of CO_2 production to O_2 consumption depends on the reaction stoichiometry, which is a function of the substrate and the state of the biomass. In the respirometer, the carbon dioxide is removed from the headspace with a strong alkali-like potassium hydroxide (KOH) according to the following reaction:

$$2KOH(s) + CO_2(g) \rightarrow K_2CO_3(s) + H_2O(l) \quad (2)$$

The resultant pressure drop triggers the release of a discrete pulse of

pure oxygen into the headspace of the reactor, reestablishing the original pressure. Using this technique, the respirometer can track oxygen consumption with time.

EXPERIMENTAL

A two-phase experimental approach was used to achieve the primary goals of this study. In phase 1, the respirometer was utilized to screen a series of 20 chemicals for their potential toxicity. In the second phase, a pilot plant study was conducted to assess the impact of a toxic additive on the treatment system and to validate the results of the respirometry tests.

Batch respirometry

A worst-case end-of-pipe concentration was calculated by assuming that all of the added chemicals passed through to the process sewer. In practice, a high percentage of paper additives are retained in the sheet, so this approach inflates the final effluent concentration for the chemical under consideration. A fluorescent-dye tracer study was also conducted in the mill to verify that this approach—based on the chemical load to the paper machine—could be used to approximate chemical concentrations in the wastewater feeding the biological treatment plant.

Effluent was collected at the inlet to the biological treatment system while the paper mill was producing standard white newsprint. The collected effluent was then frozen for use in the respirometry screening experiments. This procedure ensured a representative, reproducible food source with a minimum of papermaking additives throughout the experimental regime.

All chemicals were used as supplied by the vendor and screened in the respirometer at 10 times the estimated final effluent concentration. This high dosage was selected to accommodate the logarithmic nature of many dose–response relationships and to offset the effects of adsorption onto the biomass. This approach also ensured that any potential subtle effects would be detected. Finally, high chemical dosages also had the added benefit of providing insight into the effects of accidental releases, such as spills.

Four 500-mL reactors can be operated simultaneously in the respirometer (Comput-RX 00-240, N-CON systems, Larchmont, NY). Each reactor receives independent oxygen delivery from a compressed oxygen source, regulated to 70 kPa. A personal computer equipped with data-acquisition software (N-CON systems) and an input/output interface collected and logged all oxygen consumption and experimental conditions.

A batch respirometry method was developed and tested for screening chemicals. All four reactors received identical amounts of wastewater and biomass, with two of the reactors also receiving the test chemical. This pairing setup allows comparison both among and between the two controls and the two test samples while providing a built-in test of significance for any differences between the control and test samples. This internal standard increases the precision of the test and normalizes for day-to-day biomass variability.

Biomass was obtained from the return activated-sludge (RAS) line of the full-scale treatment system each day and aerated for 2 hours to ensure stable endogenous respiration. The frozen wastewater was thawed, filtered through a 1.2-µm glass-fiber filter (Whatman 934-AH), and adjusted to pH 8.0 prior to use to eliminate the suspended solids, ensuring a homogeneous, reproducible substrate source. Wastewater and biomass were blended such that the total suspended solids (TSS) in the respirometer reactor was approximately 2000–2500 mg/L. This biomass concentration—comparable with the mixed-liquor suspended solids (MLSS) concentration used in the aeration basin at the full-scale treatment plant—provided a linear oxygen uptake rate (OUR) well within the oxygen-delivery capacity of the respirometer at food-to-microorganism (F/M) ratios typically encountered in the treatment system.

All respirometer tests were carried out for 20 hours to simulate the hydraulic retention time in the full-scale treatment system. The reactors were submerged in a water bath controlled to 25 ± 0.1°C, which is at the low end of the temperature range for the full-scale system (25–35°C).

Continuous pilot plant studies

The pilot plant was configured to emulate the full-scale treatment system as closely as possible. Two parallel treatment trains, each consisting of two aeration basins (continuously stirred tank reactors) in series and a final clarifier, were fed from a common feed tank (the equalization (EQ) basin). Biomass from the full-scale system was used to inoculate both pilot plant trains. The pilot and full-scale systems treated the same wastewater and had similar hydraulic designs, with an overall hydraulic retention time of 24 hours.

The EQ basin (polyethylene, 100-cm diam, 110 cm high, overflow at 800 L) was agitated with an outboard mixer (Greey Mixing Equipment Ltd., Toronto, ON) and aerated to promote good mixing of nutrients, to strip off any noxious gases, and to oxygenate the wastewater before mixing with the RAS. By adding nutrients to the EQ basin, both treatment trains could be fed from a single source. Most of the feed to the EQ overflowed into a sewer connected to the full-scale treatment system.

The first aeration basin (polyethylene, 75-cm diam, 250 cm high, level control at 550 L) in each train was fed from the EQ basin using a pump

Use	Chemical name	Description	Chemical concentration, mg/L	Effect on OUR, * %
Paper dye	Red A	Basic violet 10 (Rhodamine)	710	–8
Paper dye	Green 1	Basic green 4 (Triphenylmethane)	400	–8
Paper dye	Orange 3	Similar to basic orange 2 (Azo mixture)	750	–61
Paper dye	Violet 3	Basic violet 3 (Triphenylmethane)	400	–19
Paper dye	Blue 5	Basic blue 26 (Triarylmethane)	750	53
Paper dye	Brown 4	Similar to basic brown 1 (Azo)	2950	48
Paper dye	Yellow 4	Basic yellow 78 (mixture)	1430	–13
Paper dye	Violet 5	Basic violet 3 (Triphenylmethane)	580	–45
Paper dye	Red B	Basic red 12 (Methine)	400	–42
Paper dye	Orange 5	Basic orange 63 (Methine)	870	46
Paper dye	Orange 6	Basic orange 60 (Methine)	410	–13
Paper dye	Red C	Basic red 49 (mixture)	430	–15
Paper dye	Red D	Basic red 14 (mixture)	1590	–5
Retention aid and pitch dispersant	…	Cationic latex polyelectrolyte	130	–2
Retention and drainage aid	…	Polyamine cationic polymer	400	0
Antifoam	…	Water-based antifoamer	17	2
Sizing agent	…	Cationic rosin size emulsion	400	22
General purpose cleaner	…	d-limonene, nonylphenol ethoxylate	400	–35
Microbiocide	…	Carbamate-based biocide	10	–83
Organic opacifier	…	Cationic polyamide polymer	1150	1

* Percent difference between the average oxygen uptake rate (OUR) of the controls and the test samples

I. Summary of respirometer screening tests

(Moyno Pump, Robbins & Myers Inc., Model No. 22502) at a rate of 1 L/min through polyethylene tubing (13-mm ID). Immediately before entering the first aeration basin, the feed was combined with the RAS pumped (Robbins & Myers Inc., Model No. 22002) from the underflow of the clarifier (PVC, 60-cm diam, 60-cm cylinder, 60-cm cone, 200-L volume). The wastewater flowed from the first aeration basin to a second identical basin (and to the clarifier in each train) through polyethylene tubing (25-mm ID) without further pumping. Connection ports for a fresh-water hose (350 kPa) were located between each tank for routine flushing of all hoses.

Nutrients and chemicals were added (experimental system during perturbation) using metering pumps (Alldos Pumps, Model Nos. M201-8027 and M201-4014). Nitrogen was supplied as a urea solution (150 g urea/L). Phosphorous was supplied as dilute phosphoric acid (30 times dilution of 75% H_3PO_4). Air was supplied by an electric air compressor (575 V, 20 kW, 212 m^3/h, 620 kPa) regulated to 150 kPa. Flow rate into each aeration basin and the EQ basin was controlled using ball valves. Moisture (oil in water emulsion) was continuously removed from the air header using a standard liquid separator. Coarse bubble aeration was achieved using a coiled, perforated garden hose anchored to the bottom of each tank with a stainless steel ring.

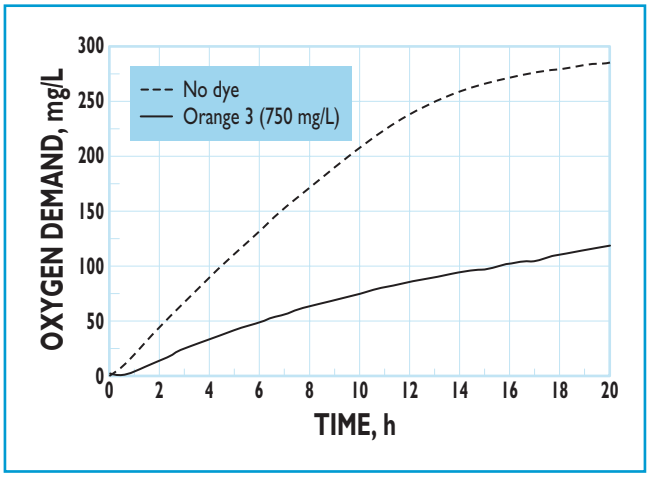
Twice per day, samples from each of the four aeration basins, the EQ basin, and the final treated effluent from each system were taken for analysis. Samples were analyzed for pH, TSS, OUR, and chemical constituents, including total dissolved carbon (TDC), phosphate as PO_4^{3-}, and nitrogen as NH_3, NO_2^-, NO_3^- *(3)*. Settling characteristics of the sludge were measured using the sludge volume index (SVI) *(3)*. The health of each culture was assessed on a qualitative basis using microscopic analysis *(4)*. Key criteria were relative abundance (many vs. few) of different organisms and floc structure (small/tight vs. large/loose). Details of the experimental procedure are given elsewhere *(5)*.

RESULTS AND DISCUSSION

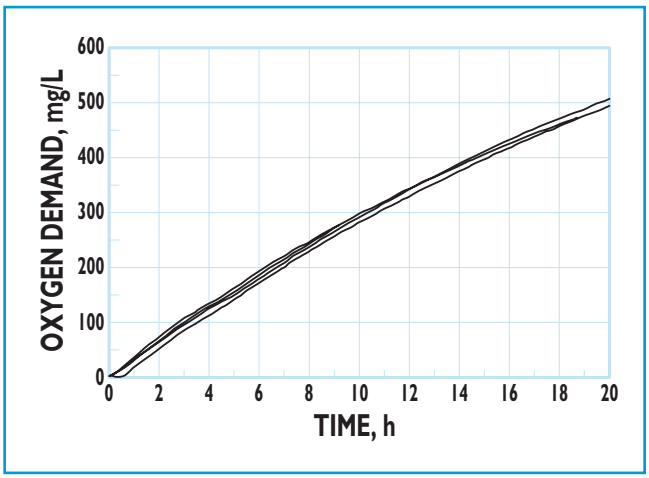
Respirometry screening tests

Results of screening tests for the 20 paper additives are presented in **Table I**. The OUR data show that many of the additives (those with high negative values) are potentially toxic to biomass. The oxygen uptake curves in **Fig. 1** illustrate the effect of a toxic dye (Orange 3) in the respirometer.

Based on replicate runs, OUR changes greater than 10% were statistically significant at the 95% confidence level. Table I shows that three dyes—Orange 3, Violet 5, and Red B—were responsible for large inhibitions to OUR. The results also suggest that a cleaning solvent could be a hazard to the activated-sludge treatment system (35% inhibition). As expected, the microbiocide was clearly toxic (83% inhibition) to the microorganisms of the effluent treatment system. The microbiocide was included to provide a benchmark for the relative toxicity of paper additives.



1. Cumulative oxygen uptake as a function of time for respiring biomass from the full-scale activated-sludge treatment system with and without addition of Orange 3 dye



2. Cumulative oxygen uptake as a function of time for respiring biomass from the full-scale activated-sludge treatment system (replicate results for four reactors)

The controls and tests were paired within each experimental run. This approach served as a built-in check for experimental errors and/or equipment problems. It also demonstrated the internal consistency of the screening tests while increasing the sensitivity of the analysis, since there were two observations for each set of conditions. The experimental precision for each run is apparent, and the significance of results could usually be determined by inspection.

The results in **Fig. 2** for four replicates (all four reactors) illustrate that the data were highly reproducible.

Biomass activity during the screening experiments can be ascertained by the relative OURs of the control and the test samples as well as by the shapes of the oxygen uptake curves. Figures 1–4 show several variations in the shapes of the curves depicting cumulative oxygen uptake vs. time.

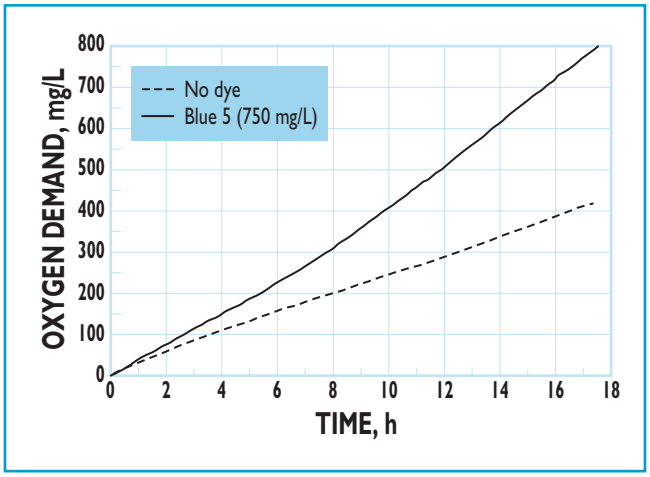
Figure 1 depicts a typical oxygen uptake curve in the absence of a toxic chemical and in the presence of Orange 3 paper dye (750 mg/L). The respiration rate of the biomass was significantly reduced with the addition of Orange 3. In contrast, the curve for the dye-free control shows a brief lag period (less than 30 min), a steep linear region (constant OUR), and a period where the OUR gradually decreases. This characteristic shape is a result of the natural metabolic cycle of the microorganisms in the activated sludge.

The microorganisms first need to acclimate to the wastewater and synthesize digestive enzymes before they can begin oxidizing substrate, resulting in a lag period. The duration of this lag period can serve as an indicator of chemically induced respiratory impacts. However, the reliability of this lag is questionable in cases when data are recorded only at 30-min intervals.

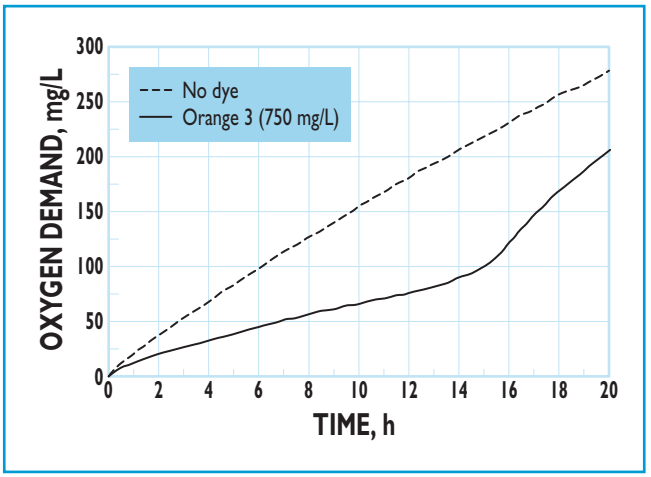
The region where OUR increases steeply corresponds to substrate oxidation by the respiring organisms. After a period of 8–10 hours, the oxygen uptake rate usually starts to decrease, indicating that the soluble food sources have been depleted and that the biomass is engaging in endogenous respiration.

Figure 3 shows that addition of 750 mg/L of Blue 5 paper dye caused a significant stimulation (53%) of the OUR and that the OUR increased with time. However, microscopic examination revealed accompanying rotifer and protozoa toxicity. This indicated that the blue dye was not a nutrient but, rather, a potential threat to the activated-sludge treatment system. One possible explanation for this seemingly contradictory observation is that blue dye may act to uncouple oxidative phosphorylation, the process by which ATP is produced. Oxidative phosphorylation is normally tightly coupled to oxygen uptake. Certain chemicals, such as 2,4-dinitrophenol and carbonyl-cyanide-p-trifluoro-methoxyphenylhydrazone, uncouple ATP production from respiration such that the microorganism continues to respire (consuming its own cell components) without securing any energy from degradation, and therefore cannot synthesize new cells *(6, 7)*. This shows that respirometry results alone can be misleading, which is why they should always be accompanied by microscopic examinations.

In most experiments using orange dye (e.g., **Fig. 4**), there was a dramatic decrease in the OUR before a sudden increase after about 15 hours. This observation has been called a death/recovery phenomenon because the biomass makes a remarkable recovery after an initial period of severe inhibition. Indeed, the respiration rate after the "recovery" exceeded that of the control. The first notion might be that the biomass suffered an initial decline, after which it became acclimated to the toxic dye and began to metabolize



3. Cumulative oxygen uptake as a function of time for respiring biomass from the full-scale activated-sludge treatment system with and without addition of Blue 5 dye



4. Cumulative oxygen uptake as a function of time for respiring biomass from the full-scale activated-sludge treatment system with and without addition of Orange 3 dye. Toxicity from Orange 3 dye (750 mg/L) was typically followed by an apparent recovery after about 15 hours.

the substrate. However, several studies by Tabak and coworkers *(8, 9)* suggest that acclimation to toxic substances can take days or even weeks. Moreover, this scenario does not account for the greater-than-normal OUR following the toxic shock.

Microscopic examination revealed carcasses of protozoa and rotifers, suggesting a rapid kill of higher life forms. This would imply some degree of bacterial toxicity corresponding to the observed OUR inhibition. When the OUR began to increase, there was a bloom of bacteria and only carcasses of protozoa and rotifers. The most probable explanation is that dead cells lyse, and their subsequent consumption by the surviving organisms is responsible for the increase in the oxygen uptake rate. Another factor that mitigates the effect of the dye is the physical adsorption of the dye. Adsorption is thought to be an important dye-removal mechanism, and this process could reduce the free dye to a subtoxic concentration. Thus the surge in OUR may reflect the activity of surviving single-celled bacteria consuming soluble organic material without dye-induced inhibition or predatory action by higher life forms.

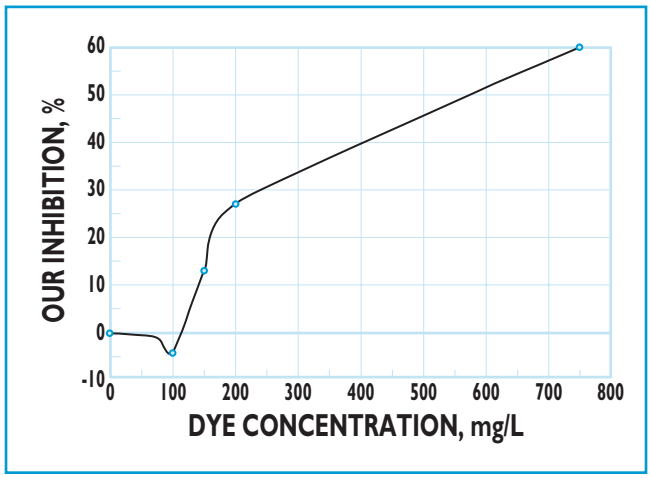
Four replicates were performed using orange dye over a period of several months. Inhibition of the biomass was consistently about 55–60% at 750 mg/L of orange dye. Repeated tests using mill effluent from the mill's stone groundwood/high-yield sulfite fiber line and the thermomechanical pulp fiber line imply that the source of the BOD has no significant bearing on the chemical's impact on the respiration rate of the biomass.

Sensitivity to the paper dyes during respirometer screening was dependent on the amount of biomass present. At lower biomass concentrations, the toxicity of dyes increased significantly, suggesting that toxicity can be reduced through physical adsorption to biomass. If this is the case, then the key to sensitivity may be the mass of material available to adsorb toxins.

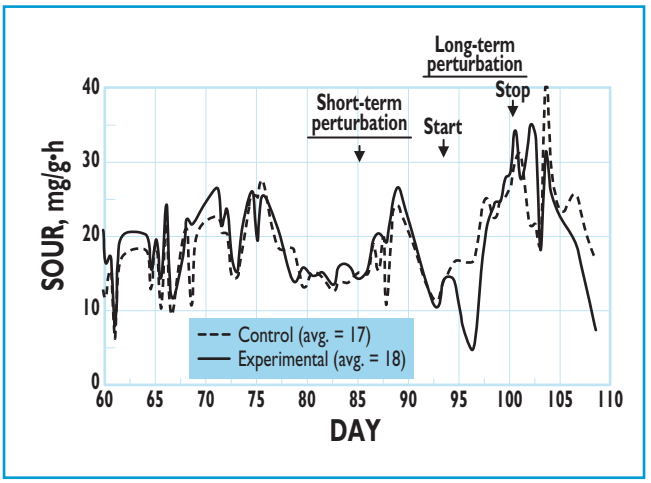
Inert material may also act as a buffer for toxic upsets if the toxin is highly physically adsorbed. In this case, the toxin is a cationic paper dye and the inert material is anionic paper fibers, so physical removal is expected to be efficient and irreversible. To obtain the most realistic measure of a chemical's potential to influence respiring microorganisms under a shock load, a standard screening procedure should use biomass concentrations as close to full-scale conditions as possible, without exceeding the oxygen-transfer limitations of the respirometer.

Respirometer screening and pilot plant results indicate that paper additives are toxic at very high concentrations, but they are unlikely to cause significant effects under normal operations. The worst offender was an orange dye (Orange 3), which inhibited the OUR by 61% at a concentration of 750 mg/L. An inhibition of this magnitude represents a severe toxic shock that would likely cause failure of the treatment system. However, the screening concentration of 750 mg/L is 10 times the estimated worst-case effluent concentration, which assumes that no dye is retained in the paper. The dose–response curve for Orange 3 in **Fig. 5** shows that significant respirometric inhibition does not begin until approximately 150 mg/L. This curve is typical of many dose–response relationships, which demonstrate a sharp increase in toxicity beyond a critical concentration before asymptotically approaching an upper limit.

Respirometer screening at 75 mg/L (the worst-case concentration) showed that there was no negative impact on the respiration rate of activated sludge. Further, considering that approximately 80% of the paper dyes added to the stock become part of the finished paper product, it is clear that the activated-sludge system at Iro-



5. Dose–response curve for Orange 3 dye using respiring biomass from the full-scale activated-sludge treatment system



6. Pilot plant operating data showing specific oxygen uptake rate (SOUR) in the first aeration basin after addition of Orange 3 dye during a short-term perturbation (750 mg/L for 2.4 h) and a long-term perturbation (200 mg/L for 7 days)

quois Falls is in little danger from toxicity due to normal dye consumption (2–50 kg dye/metric ton paper) in the paper mill.

The biological effluent treatment system at Iroquois Falls has experienced many extended exposures to paper dyes without loss in treatment performance. However, there are always some subtle changes in the treatment system (e.g., colored foam, slight dispersed growth). But without specific and explicit documentation, these observations are not captured in routinely monitored process parameters. Hence, the significant inhibitions observed in respirometer tests (at 10 times the normal concentration) suggest that there are small impacts to the biomass at lower doses. However, these smaller impacts are not observable with the screening test.

Milanova *et al. (10)* reported toxicities of newsprint dyes to activated sludge. Their results were comparable with those observed in this work, and they similarly concluded that normal effluent concentrations should be noninhibitory. However, Brown *et al. (11)* reported IC_{50} (inhibiting concentration for 50% of test organisms) values of 10–100 mg/L for the three dyes—Orange 3, Violet 5, and Red B—that showed the greatest toxicity in this study. The concentrations reported by Brown *et al. (11)* suggest that oxygen uptake could be inhibited under normal mill operation. Since the same chemicals were found to be toxic in both of the cited studies, the difference in the results may be due to the source of the biomass: Milanova *et al. (10)* used biomass from a TMP mill, while Brown *et al. (11)* used biomass from a municipal treatment plant. The biomass used by Brown *et al. (11)* was probably more sensitive to inhibition by paper dyes because it was totally unacclimated. This is consistent with the findings of Moebius and Demel *(12)*, who found that normal effluent from various paper mills was toxic to unacclimated biomass from a municipal treatment system.

Pilot plant studies

The pilot plant was operated for a period of three months to establish stable operation and to demonstrate that the two parallel pilot treatment systems behaved in a similar and predictable manner.

The experimental train of the pilot plant was perturbed twice by adding Orange 3 dye. The short-term perturbation (750 mg/L for 2.4 hours) was equivalent to a slug of dye entering the treatment system. The long-term perturbation (200 mg/L for 7 days) was equivalent to a period of extensive dye consumption in the paper mill.

Figure 6 shows the trend for specific oxygen uptake rate (SOUR) in the first aeration basin of the two treatment trains from days 60–110.

There were no observable changes in the pilot plant after the short-term exposure to high dye concentration (day 85), an indication of the treatment system's ability to assimilate shock loads. There may have been some small toxicity as the RAS and dye were mixed, but upon entering the first aeration basin, dilution and adsorption would have decreased the dye concentration considerably. During such a short time, only about 10% of the biomass would come into contact with the inhibitory dye concentration.

Continuous exposure to orange dye during the second pilot plant perturbation (days 93–100) resulted in a 72% decrease in SOUR in the first aeration basin (Fig. 6) and a 52% SOUR decrease in the second aeration basin by the third day. These levels of inhibition were approximately twice as great as predicted by the batch tests. The heightened response in the pilot plant biomass during continuous flow exposure may be due to saturation of the biomass by the dye, which does not occur in batch tests.

Extended dye exposure also led to other impacts that were not predicted by respirometry. Effluent solids losses increased due to dispersed growth and the nature

of the pinpoint floc produced from this growth condition. The settling characteristics of the sludge also appeared to deteriorate, as suspected denitrification caused biomass to float in the clarifier. Foaming, indicative of toxicity, also increased after extended dye exposure. This same type of foam has been observed at the full-scale plant startup and after extended dye consumption in the paper mill.

Ammonia residual decreased while nitrite and nitrate residuals increased, such that the total nitrogen residual in the experimental train was twice that in the control. The reduced ammonia residual may have been due to rapid growth of new bacteria, but it is more likely the result of partial oxidation of ammonia nitrogen to nitrite. The increased nitrite and nitrate residuals are not fully understood. Pagga and Brown *(13)* suggest that the dyes are not broken down by activated-sludge organisms and probably do not themselves release nitrogen. This implies that the nitrogen must originate from increased cell lysis associated with dye toxicity. Since conversion of ammonia nitrogen to nitrite is the rate-limiting step in the two-step nitrification process by *nitrosomonas* and *nitrobacter*, it is possible that the paper dye selectively inhibited the activity of *nitrobacter*, thereby slowing the conversion of nitrite to nitrate *(14)*. Elevated nitrite levels may lead to effluent toxicity, whereas excess nitrate may lead to denitrification with an inversion of the secondary clarifier and excess solid losses.

The final effect of the orange dye on the pilot plant, not predicted by respirometry, was the dramatic darkening of the biomass and the final treated effluent. This observation is indicative of the extensive adsorption of dye onto biomass. Sludge darkening is often observed in the full-scale system, especially after producing black construction paper, but never to the extent seen in the pilot experiments. Slight coloration of the treated effluent is also observed in the full-scale system, a reminder of the recalcitrant nature of paper dyes.

The screening method employing batch respirometry was able to predict process upsets in the continuous flow pilot plant and is therefore applicable to full-scale treatment systems. The principal upsets predicted by respirometry are a dramatic decrease in SOUR and a microbial population shift as higher life forms are killed and single-celled bacteria dominate.

Respirometer screening tests with polymers used in papermaking indicated that these large molecules did not impact the respiration rate of the biomass. Microscopic examination confirmed that there was no observable toxicity from these compounds. Given the high molecular weight (ca. 1–2 million g/mole) of these macromolecules, it is unlikely that they would be bioavailable, thereby rendering them inactive as toxicants.

Application to the pulp and paper industry

The proposed batch respirometry test is a reliable method of prescreening papermaking additives to evaluate their potential effects on the stability of downstream biological effluent treatment systems. Test results can be used to regulate the use of chemicals in the mill (i.e., which chemicals, when, and how much) and to predict the potential for process upsets in the event of a chemical spill. If the screening tests indicate a potential for system perturbation, then the mill can follow up by challenging chemical suppliers to provide less toxic products. Test results can also help the mill identify situations when the effluent treatment system needs to be fortified to accommodate production of papers requiring large amounts of chemical additives.

Ideally, all chemicals on the mill premises should be screened for their potential impact on the activated-sludge effluent treatment system.

CONCLUSIONS

Batch respirometry is a reliable method for screening the impacts of papermaking additives on activated-sludge effluent treatment systems. The proposed method is rapid, providing reproducible results within two hours. Moreover, the test is sensitive enough to detect chemically induced changes of 10% in the respiration rate of the treatment system biomass.

However, respirometric measurements also have some disadvantages. Physical changes in the biomass (e.g., settling characteristics) are not detected by measuring oxygen uptake rates. Such changes can only be evaluated with a continuous pilot plant treatment system. In addition, conclusions based exclusively on respirometry can be misleading if a chemical stimulates the oxygen uptake rate through uncoupling of oxidative phosphorylation.

Qualitative microscopic examinations are valuable in assessing the toxicity of chemicals and should be included as part of the standard screening test. Microscopic evidence of toxicity to indicator organisms (e.g., rotifers and protozoa) can reveal subtle effects not observed with respirometry and may help in identifying possible uncoupling effects.

Some chemicals that are toxic to activated sludge at high concentrations are nontoxic at normally expected mill effluent concentrations. Of the papermaking additives tested, paper dyes were found to be most toxic, with orange, violet, and red causing the highest inhibitions to the respiration rate of the biomass. Other process additives, such as a

general purpose cleaner/solvent and a microbiocide, also exerted a significant toxicity to activated sludge.

Adsorption of dyes by biomass is an important toxicity removal mechanism. Sensitivity to dyes increases with decreasing biomass concentration, and it may also increase with extended dye exposure as the biomass becomes saturated and adsorption less effective. **TJ**

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