Oxidation–Reduction Potential Changes in Aeration Tanks and Microprofiles of Activated Sludge Floc in Medium- and Low-Strength Wastewaters

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ABSTRACT: Real-time control of aeration tank operation is key to high-efficiency pollutant removal and energy savings. One of the aims of this study was to examine the potential for using redox potential (oxidation–reduction potential [ORP]) to indicate wastewater quality online in aeration tanks treating medium (chemical oxygen demand [COD] of 70 to 150 mg/L) and low (COD of 15 to 30 mg/L) pollutant-concentration wastewaters. The field-scale data provide a good relationship between ORP values and nutrient removal along the length of the aeration tanks. The ORP values increased dramatically as organic matter was removed along the aeration tanks, indicating the improvement of the bulk liquor redox status. Dissolved oxygen higher than 1.0 mg/L was necessary for good biodegradation and improvement of the liquid redox status. Nitrification occurred at higher ORP values (380 to 420 mV) than was the case for organic substrate oxidation (250 to 300 mV). The microprofiles obtained from microelectrode measurements substantiate the heterogeneity of the microbial processes inside activated sludge flocs. Because of microbial oxygen utilization, the aerobic region in the activated sludge floc was limited to the top layer (0.1 to 0.2 mm) of the activated sludge aggregate present in medium-strength wastewater, with an anoxic zone dominating inside the flocs. When dissolved oxygen in the bulk water was higher than 4.0 mg/L, the anoxic zone inside the floc disappeared. At low wastewater pollutant concentrations, the ORP and dissolved oxygen inside the activated sludge aggregates were higher than those from medium-strength wastewater. The prospect of using ORP as an online control approach for aeration tank operation and the potential reasons for activated sludge floc size varying with pollutant strengths are also discussed. *Water Environ. Res.*, **76,** 394 (2004).

KEYWORDS: redox potential, oxidation–reduction potential, aeration tanks, activated sludge floc, microelectrode, microenvironment, nutrient removal, dissolved oxygen.

Introduction

Biological nutrient removal (BNR) using activated sludge processes is accomplished through the uptake of pollutants by microorganisms retained in the activated sludge floc or by those free-living in the bulk wastewater. Many biochemical reactions are involved in the biodegradation. Recent advances in BNR processes have indicated that the incorporation of unaerated zones can be beneficial to the process economics (Dold and Marais, 1987). These benefits include less energy required, less sludge production, and a more stable denitrification. Anaerobic, anoxic, and aerobic (AAA) integrated processes have been used for phosphorous removal. Biological nutrient removal is achieved by aerobes, nitrifiers, denitrifiers, and phosphorous-accumulation organisms in aerobic, anoxic, and anaerobic environments. To optimize the activated sludge process, especially AAA processes, an easy-to-use online parameter should be available to reflect the real-time respiratory states under anoxic and even anaerobic conditions. Most wastewater treatment processes still use dissolved oxygen (DO) control for aeration tanks, which neglects the metabolism of the microorganisms involved. One evident problem of using DO control in an anoxic or anaerobic process is that DO readings become unreliable when DO is below 0.1 to 0.2 mg/L (Moriyama et al., 1993).

In the past two decades, research has been conducted to achieve more efficient control of activated sludge processes. Use of oxidation–reduction potential (ORP) has gained broad attention as a control parameter for wastewater treatment systems. The ORP value is a measure of the tendency of a given system to donate electrons (oxidizers) or receive electrons (reducers) involved in solutions. For aerobic biological wastewater treatment systems, free oxygen, nitrite, and nitrate are typically the oxidizer species in aeration tanks; the biomass and many organic pollutants are typically the reducers. Oxidation–reduction potential values vary with the concentrations of oxidant and reductant in solution. Findings show that ORP can be used as a control parameter in all three respiratory states: aerobic, anoxic, and anaerobic (Al-Ghusain et al., 1994; Yu et al., 1997). Simultaneous nitrification and denitrification may occur when the ORP is 118 to 150 mV (silver/silver chloride [Ag/AgCl]), even though DO may be only 0.1 to 0.3 mg/L (Moriyama et al., 1993). Peddie et al. (1990), Yu and Bishop (1998), and Yu (2000) pointed out that in most complex biological systems, such as wastewater biofilms and activated sludge, many chemical and biological oxidation–reduction reactions take place together. Moreover, the reactions are not in equilibrium and the measured ORP values cannot be interpreted thermodynamically. The measured ORP is an overall result of the microbial and chemical activities of every component in the system during testing. The ORP values comprehensively represent the redox-potential level of all the biochemical reactions in the system. From the ORP definition formula, the higher the concentrations of the reductive compounds, the lower the ORP values. Based on this feature, ORP can be used to indicate the wastewater quality at different treatment phases.

Online ORP monitoring has proven to be a practical technique for controlling the activated sludge process, sludge digestion, BNR, and chemical oxidation–reduction processes (Chang et al., 1994; Lo et al., 1994; Peddie et al., 1990). Some authors, including Rimkus (1985), have used the absolute ORP values for control purposes. Other authors, such as Koch and Oldham (1984) and Wareham and

Table 1—The wastewater quality of plant influent and effluent at two plants.

	COD (mg/L)	TKN (mg/L)	NH_4^--N (mg/L)	NO_3^--N (mg/L)	MLSS (mg/L)	pH	HRT (hour)	SRT (day)	Aeration mode
Aeration tank influent									
Mill Creek Plant (Treatment capacity: 120 mgd)	65 to 150	30 to 40	10 to 30	0 to 0.2	2000 to 3000	6.7 to 7.2	6	3 to 6	Alternate air-on/air-off
Muddy Creek Plant (Treatment capacity: 14 mgd)	20 to 40	10 to 20	10 to 15	0 to 0.3	1700 to 2400	6.9 to 7.2	4	13 to 17	Constant aeraion
Secondary settling tank effluent									
Mill Creek Plant	10 to 30	15 to 20	10 to 15	0.5 to 3		6.5 to 7.0			
Muddy Creek Plant	2 to 4	1 to 3	0.2 to 0.8	5 to 15		6.5 to 7.0			

Hall (1993), have favored wastewater control strategies based on the relative change in ORP with time. Besides the advantage of ORP control over DO control under anoxic or anaerobic conditions, ORP has another significant advantage; as an indicator of the redox status of wastewater, ORP can comprehensively indicate many factors in wastewater such as chemical oxygen demand (COD), DO, and changes in nitrate (NO_3^-) or ammonium (NH_4^+) concentrations. In activated sludge systems, many biological substances such as enzymes and vitamins and most metabolic processes are redox systems and correlate strongly with ORP values. Oxidation–reduction potential real-time controls in a full-scale plant can not only provide for carbonaceous and nitrogenous material removal with good performance, but they can also conserve as much as 20% of the energy cost (Charpentier and Florentz, 1987). Therefore, achieving ORP control in a wastewater treatment plant (WWTP) has economic importance.

In the process of biological wastewater treatment, microbial communities are retained in aeration tanks via accumulation in flocs or aggregates. Electron acceptors (oxygen) and donors (soluble substrates) are subject to mass-transfer limitations inside activated sludge flocs. Gradients around and inside activated sludge flocs are maintained by the balance between the bacterial uptake (utilization rate) and diffusion of the compounds (renewal rate) from the bulk solution. The removal of substrate and diffusion of oxygen from the proximity of the cells leads to the establishment of a patchy microenvironment characterized by several dynamic gradients (Takacs and Fleit, 1995). The metabolic activity of microorganisms is directly correlated with excess sludge production in the aeration tanks. Some models of oxygen and substrate profiles inside activated sludge floc have been developed (Abbasi et al., 2000; Takacs and Fleit, 1995). Using models, it has been calculated that the DO concentration can drop to low levels in the core of floc, even under normal operating conditions, and substrate concentrations can begin to increase in the direction of the floc core. There is little research on the microenvironment of activated sludge (De Beer et al., 1998), and direct proof of the changes of spatial stratification inside activated sludge flocs in different wastewaters has not been reported. In this study, microelectrode techniques were used to investigate the ORP status inside activated sludge flocs to verify the presence of anoxic processes existing under aerobic conditions and to determine dynamic differences inside flocs between the aeration tank influent and effluent.

Literature indicates that most ORP control research has been conducted only at lab- or pilot-scale (Bertanza, 1997; Charpentier and Florentz, 1987; Heduit and Thevenot, 1989; Koch and Oldham, 1984; Peddie et al., 1990; Schon and Geywitz, 1993; Zhao, 1998). Most of this research has concentrated on the simultaneous nitrification–denitrification process. Although ORP control for COD removal has been monitored in a few research projects (Charpentier et al., 1998; Yu and Lo, 1994), the ORP and COD relationship in aeration tanks has not yet been thoroughly examined. Moreover, because of difficulties in immobilizing individual activated sludge floc particles during measurements, little research has been reported on the ORP of the microenvironment of activated sludge flocs in different quality wastewaters (De Beer et al., 1998).

This research consisted of two parts. The first part was a full-scale study of the aeration tanks at two WWTPs in Cincinnati, Ohio: the Mill Creek Wastewater Treatment Plant and the Muddy Creek Wastewater Treatment Plant. The purpose of the study was to investigate and develop strategies for ORP regulation of organic removal from aeration tanks for wastewaters with different COD ranges. The relationship between ORP, COD, and DO along the length of the aeration tanks was established based on on-site measurements. The second part of the study involved microprofile measurements of activated sludge floc taken from these two wastewater treatment plants. With the use of microelectrodes (DO, pH, NH_4^+, NO_3^-, and ORP), the spatial stratification of microbial processes inside the activated sludge floc was investigated and the effects of bulk DO concentration and substrate concentration on the microprofiles in the sludge flocs were determined.

Materials and Methods

Plant Description. The research fieldwork was carried out at two municipal plug-flow WWTPs in Cincinnati, Ohio: the Mill Creek Wastewater Treatment Plant and the Muddy Creek Wastewater Treatment Plant. Typical aeration tank water quality at the two plants is shown in Table 1. The Mill Creek treatment facility is the largest of 26 treatment plants operated by the Metropolitan Sewer District of Greater Cincinnati. The influent to the wastewater treatment facility is composed of 70% industrial wastewater and 30% municipal wastewater. The plant has a design capacity of 5259.6 L/s (120 mgd) flow and a peak flow capacity of 13 149 L/s (300 mgd). There are six aeration tanks in parallel that provide detention time and aeration for the mixed liquor. The hydraulic retention time (HRT) in each aeration tank at design flow is six hours. The COD and ammonium concentrations for the aeration tank influent during this study were 65 to 150 mg/L and 10 to 30 mg NH_3-N/L, respectively; minimal nitrification or denitrification occurred in the aeration tanks. Currently, aerator operation depends on DO control. Intermittent aeration has been used in the aeration tanks since the summer of 1998 (Aman and Bishop, 1999). The wastewater is aerated for a period, and then the air supply is decreased for a short period so that the bacteria effectively use the supplied air. The ideal situation appears to be aeration, with aerator "on" and "off" cycles of 30 minutes each.

The treatment capacity of the Muddy Creek Wastewater Treatment Plant is 613.62 L/s (14 mgd). The source of the wastewater is primarily municipal wastewater. Aeration is kept on continually along the two parallel aeration tanks. The HRT in each aeration tank at design flow is four hours. The COD and ammonium concentrations for the aeration tank influent during this study were 20 to 40 mg/L and 10 to 18 mg NH_3-N/L, respectively. Significant nitrification occurred in the aeration tanks. Nitrate concentrations in the effluent were 5 to 15 mg NO_3^--N/L.

Oxidation–Reduction Potential, Dissolved Oxygen, and Oxygen Uptake Rate Measurements in Aeration Tanks. The full-scale research period was from December 1999 to July 2000, with sampling occurring from 10:00 a.m. to 2:30 p.m. twice a week. An Orion (Beverly, Massachusetts) multifunction portable meter (model 1230) was used for on-site measurement of the DO, pH, and ORP in the aeration tanks. The Orion ORP sensor (model 9678) consists of an epoxy body with a sleeve junction and combines a platinum redox and Ag/AgCl reference electrode in one body. The ORP electrode was cleaned with deionized water and calibrated with freshly prepared potassium ferrocyanide–potassium ferrictanide–potassium fluoride buffer solution (ORP values of 234 and 300 mV [Ag/AgCl]; Orion, 1997) before every use. The ORP values reported here are the standard hydrogen redox values (Eh), which were converted from the measured ORP values (Ag/AgCl) by adding 200 mV. No detectable difference in water quality with depth in the aeration tanks was observed. The position of measuring–sampling points along the length of the aeration tanks was fixed during on-site measurement periods, with 36.576 m (120 ft) between each sampling point. Wastewater samples were taken from 1.524 m (5 ft) below the water surface and 0.609 (2 ft) away from the aeration tank inner wall to ensure that the water samples represented typical mixed wastewater in the aeration tanks.

The oxygen uptake rate (OUR) was measured on-site for wastewater samples taken from the aeration tanks. First, 250 mL of fully aerated five-day biochemical oxygen demand (BOD_5) buffer solution was added to a 300-mL BOD_5 bottle. Then, a 50-mL wastewater sample was added to the bottle. Samples were continuously stirred while measuring DO to maintain consistent and representative readings. An Orion DO probe was used to monitor the DO levels in the mixed solution. The decrease in DO concentration was measured every 10 seconds until the DO dropped to 0.5 mg/L. The slope of the DO concentration versus time graph was used to obtain the OUR (mg O_2/L/min).

Analyses of Aeration Tank Bulk Solution. After the wastewater sample was collected from an aeration tank, it was immediately put into a cooler and allowed to settle for five minutes. The supernatant was then filtered through a glass-fiber membrane and transferred to a 50-mL centrifuge vial to prevent the loss of COD after sample collection. The centrifuge vial was stored in a refrigerator, and COD was measured on the same day of sampling using the Hach (Hach Company, Loveland, Colorado) U.S. Environmental Protection Agency method 410.4 procedure. Acetate-Plus (GE Osmonics, Minnetonka, Minnesota) membranes (pore size of 0.45 μm) were used to filter wastewater samples to avoid the effect of suspended solids on COD measurements. The COD values presented here represent soluble COD. Duplicate measurements were made for all samples. Ammonia and pH were measured using Orion electrodes. A Dionex (Sunnyvale, California) ion chromatograph (model DX-120) with a Dionex AS14-4 mm column was used for nitrate analysis.

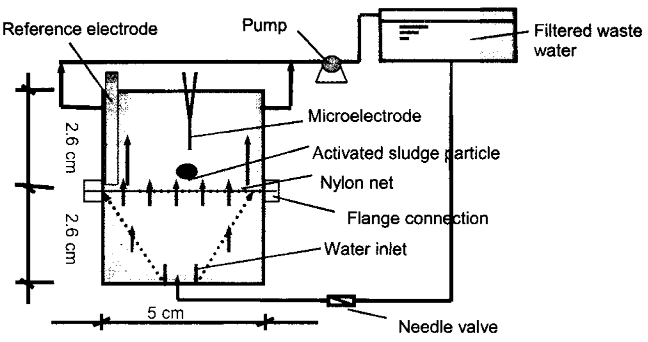

Figure 1—The upflow chamber (Ploug and Jorgensen, 1999) for microprofile measurements.

Microelectrode Techniques. Microelectrodes with tip diameters of 3 to 15 μm make it possible to monitor several metabolic reactions on a scale relevant to the study of stratified bacterial communities, such as biofilm and sediment mats (Revsbech and Jorgensen, 1986). For nitrification and denitrification studies, microsensors for nitrous oxide–oxygen (Revsbech et al., 1989), ammonia (Schramm et al., 1999), and nitrate (De Beer and Sweerts, 1988) have been developed and used for investigations in different habitats (Jensen et al., 1993). For sulfur reduction in biofilms, a sulfide microelectrode has been developed (Kuhl and Jorgensen, 1992; Yu, 2000). Dissolved oxygen microelectrodes have been used to measure the DO in the aforementioned microbial processes, and redox potential (ORP) microelectrodes were used to measure redox status changes inside biofilm (Yu and Bishop, 1998).

In this study, five microelectrodes (DO, pH, NH_4^+, NO_3^-, and ORP) were used to investigate the spatial stratification of microbial processes inside activated sludge floc from the Mill Creek and Muddy Creek WWTPs. Microelectrodes have been developed and used in our lab for more than a decade (Fu et al., 1994; Li and Bishop, 2002; Yu, 2000; Yu and Bishop, 1998; Zhang et al., 1994; Zhang and Bishop, 1994, 1996). The microelectrodes described in the following subsections were used as working electrodes. An Ag/AgCl millielectrode (Microelectrodes, Inc., Bedford, New Hampshire; no. MI 401) was used as the reference electrode throughout this study. The reference electrode was placed in the solution inside the upflow chamber (Figure 1).

Redox Potential (Oxidation–Reduction Potential) Microelectrode. Oxidation–reduction potential microelectrodes were first introduced to our lab by Yu (Bishop and Yu, 1999). The ORP microelectrode is a solid-phase electrode made from a platinum wire and low-melting-point lead glass micropipettes. It can potentiometrically measure the oxidation–reduction potentials in solutions. The detailed manufacturing procedures can be found in Yu (2000).

Dissolved Oxygen Microelectrode. The DO microelectrode is the most mature microelectrode and can be made in several ways. The DO microelectrodes made in the authors' lab are polarographic recessed gold electrodes with tip diameters of 3 to 7 μm. They measure amperometrically the DO concentrations from zero to saturation. The fabrication of the oxygen microelectrode was

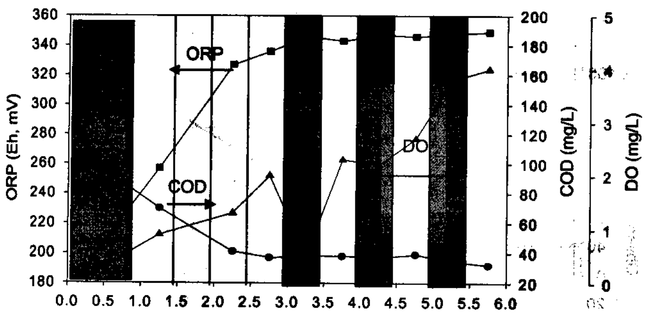

Figure 2—Chemical oxygen demand, dissolved oxygen, and ORP at West #1 aeration tank in the Mill Creek Plant (December 10, 1999).

modified by Fu (1993) and Zhang (1994) in our lab from those described by Linsenmeier and Yancey (1987).

Ammonia, Nitrate, and pH Microelectrodes. The ammonia, nitrate, and pH microelectrodes represent liquid-membrane, ion-selective electrodes with tip diameters of 3 to 5 µm. They are suitable for potentiometric measurement of ammonia, nitrate, and pH in solution. The manufacturer of the liquid membrane (ionophore) used in this research is Fluka (Buchs, Switzerland). Fluka no. 09879, no. 72549, and no. 95293 liquid membranes were used for ammonium, nitrate, and pH microelectrodes, respectively (Li and Bishop, 2002). A thin layer of cross-linked protein was applied to the microelectrode tip (De Beer et al., 1993) to prevent interference from other ions present in the measured solution. Unlike ORP and DO microelectrodes, which can last longer than two years if maintained properly, the liquid-membrane, ion-selective electrodes only last one to three days because of evaporation of the liquid membrane.

Microelectrode Calibration. After the microelectrodes were made, they were each calibrated and the best ones were selected for use in experiments. The ORP microelectrodes were calibrated in redox standard solution (ASTM D1498-93) (ASTM, 2003), with ORP ranging from 90 to 430 mV (Ag/AgCl); their performance was also compared to a commercial Orion ORP electrode. The oxygen microelectrodes were calibrated in saline solution saturated with air and nitrogen gases containing 0, 5, and 10% oxygen. The pH microelectrodes were evaluated in standard pH buffer 6, 7, and 8. Ammonium microelectrodes were calibrated in 1-, 10-, and 50-mg N/L NH_4Cl solutions, and nitrate microelectrodes were calibrated in 0.1-, 1-, and 10-mg/L $NaNO_3$ solutions. Typically, the performance of ORP and DO microelectrodes was stable throughout the experiments. The ion-selective microelectrode (ammonia, nitrate, and pH microelectrodes) readings tended to shift over time, so it was necessary to calibrate the ion-selective microelectrodes before and after experiments; any necessary corrections were made to the calibration curves (Li and Bishop, 2002).

Upflow Chamber. One reason there is little research on the microenvironment of activated sludge flocs is that it is difficult to keep the floc particle suspended in the flowing liquid, but stationary, while the microelectrode penetrates through the floc. This problem has been resolved using an upflow chamber (Ploug and Jorgensen, 1999). Figure 1 shows a diagram of the upflow chamber. The upflow chamber was made by gluing two Plexiglas tubes together (each tube was 5 cm in diameter with a length of 2.6 cm, which is shorter than that described in the literature). The height was adjusted to fit the experimental space under the microscope. A parallel, uniform upward flow, in which a floc–aggregate can be stabilized in suspension, was achieved by using nylon net that was tightly stretched and glued between the ends of the two Plexiglas tubes. The advantage of the elastic nylon net is that it is easy to make a flat surface. Water was kept flowing through the chamber to keep the floc particle in suspension. The flowrate was controlled with a needle valve. Water overflowed through four opposing outlets at the upper part of the flow chamber back to the reservoir. The reservoir (1.5 L) contained the filtered wastewater taken from the aeration tanks (filter member pore size of 10 µm). Dissolved oxygen in the filtered wastewater was adjusted to be the same as in the aeration tanks to make the environment of the upflow chamber similar to that in the aeration tanks.

Activated Sludge Floc Sample. After an activated sludge sample was taken from a Mill Creek or Muddy Creek WWTP aeration tank, it was immediately transferred to the lab for measurement. A cut pipette tip (tip diameter of 1 to 3 mm) was used to suck up one drop of the activated sludge sample. Then, the drop of activated sludge floc was gently placed just above the nylon net in the upflow chamber in which filtered wastewater was continually flowing. The diameters of the activated sludge floc tested in this study were 1.0 to 1.3 mm, which is slightly larger than that of previously reported flocs (De Beer et al., 1998; Satoh et al., 2002; Seviour and Blackall, 1999) but within the typical range of 0.1 to 1.5 mm. This slightly larger size may be attributed to the use of gentler mixing. Fourteen replicate activated sludge floc samples were measured from the influent and effluent at each WWTP, with typical profiles presented here.

Microprofile Measurements. The microprofile measurements were carried out in a faraday cage. After the activated sludge floc was observed to be in suspension just above the nylon net in the chamber, a microelectrode was located 1.0 mm (in distance) from the surface of the floc particle. The position of the microelectrode was controlled using a micromanipulator. A Nikon (Tokyo, Japan) stereomicroscope, charge-coupled device camera, and color monitor were used to monitor the location of the microelectrode during all measurements. The microelectrode readings were recorded at 100-µm intervals. The chemical profiles presented were all obtained from the same activated sludge floc under each test condition; that is, after one microprofile measurement was finished, the next profile was measured on the same floc. Although there is potential physical disturbance to floc during measurement, when microelectrodes penetrate the same floc a few times, the effect is negligible because the initial activated sludge floc is a porous entity and the diameter of the floc particle (approximately 1.0 mm) in this study is far larger than that of the microelectrode tip (3 to 10 µm).

Results and Discussion

Oxidation–Reduction Potential, Dissolved Oxygen, and Chemical Oxygen Demand Changes in Aeration Tanks at the Mill Creek and Muddy Creek Plants. *Mill Creek Wastewater Treatment Plant.* Figure 2 shows typical ORP, DO, and COD changes along the length of one of the Mill Creek plant aeration tanks. The blank area represents "air-on" zones, while the gray shaded area represents "air-off" zones. The aeration tank influent had an average COD of 100 mg/L and an ORP of 180 mV (Eh). The ORP increased dramatically when the air-on zone was reached after one hour. During the first three hours of treatment, ORP values increased from 180 mV in the influent to 338 mV, and COD decreased from 103 to 41 mg/L in the middle part of the aeration tank. The ORP increase occurred because of the increase in DO in the

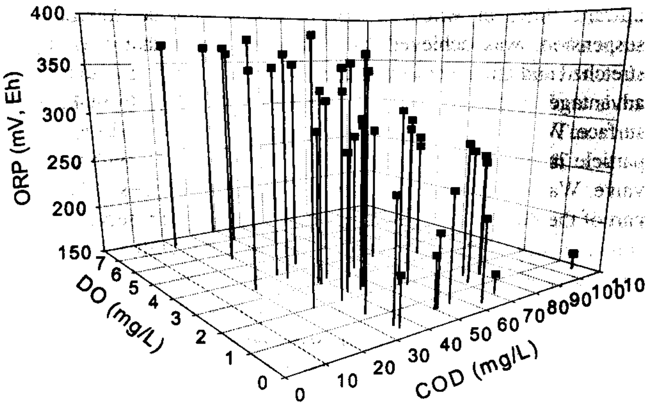

Figure 3—The effects of dissolved oxygen and COD on ORP values of aeration tank effluent in the Mill Creek plant.

mixed liquor and the substrate removal along the tank. In the second three hours of treatment, the bulk-liquid ORP increase rate and the COD decrease rate slowed down. It was deduced that the macrobiodegradation by microorganisms was almost complete in the second part of the aeration tank. Microbiodegradation inside the activated sludge flocs continued after the first three hours of treatment and further stabilized the absorbed pollutants. Effluent COD decreased to 30 mg/L and ORP increased to 349 mV, indicating the effluent was in a relatively high oxidizing status.

Different biodegradation styles for the microorganisms in the aeration tanks were derived based on the on-site experimental results, which show ORP values dramatically increased during the first three hours and then slowed down during the second three hours of treatment. During the first three hours of treatment, sorption and biodegradation of pollutants were dominant. The large molecular weight and easier-to-degrade pollutants were adsorbed and biodegraded by microorganisms suspended in the bulk liquid and fixed inside the activated sludge floc, resulting in a significant decrease of pollutant concentrations in the bulk wastewater. Bulk wastewater ORP values increased accordingly. In the latter part of the aeration tank, organic stabilization within activated sludge flocs dominated the degradation products and the adsorbed pollutants from the first three hours of treatment were biodegraded inside the activated sludge flocs. This latter microbial degradation process is necessary for complete stabilization of the waste. Because removal of pollutants from the bulk liquid was almost finished after the first three hours, the COD concentration leveled off during the second three-hour period. Wastewater ORP values slightly increased during the second three hours (from 338 to 350 mV in the effluent), with COD concentration decreasing from 41 to 30 mg/L during the second three hours. The bulk liquor ORP values approached a stable value during the second three hours of treatment.

The Effect of Dissolved Oxygen and Temperature on Oxidation–Reduction Potential and Chemical Oxygen Demand in the Aeration Tank Effluent at the Mill Creek Plant. Figure 3 depicts the COD, ORP, and DO data obtained from more than half a year of on-site measurements at the Mill Creek plant west #1 aeration tank effluent. The aeration tank effluent ORP values were below 250 mV when dissolved oxygen was lower than 1.0 mg/L, although effluent COD was sometimes as low as 40 mg/L. It should be noted that low effluent COD associated with low ORP was observed in the summer (T_{water} = 23 to 27 °C), while high effluent COD associated with low ORP was observed in winter (T_{water} = 10 to 15 °C). Hetzler and Spielman (1995) reported that ORP readings steadily decrease when wastewater temperatures increase. This is because of the lowered wastewater oxygen-saturation capacity and the greater oxygen consumption by microorganisms brought on by warmer conditions. The DO concentration in wastewater can be reflected in the wastewater ORP values. Without sufficient DO, the effluent still had a low oxidizing status.

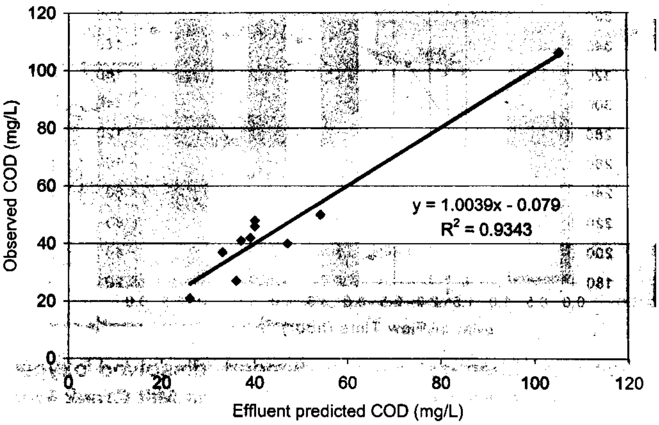

Figure 4—A comparison of predicted COD and observed COD in the aeration tank effluent at different temperatures at the Mill Creek plant.

When the DO of the effluent was increased to 2 mg/L, ORP values were typically higher than 270 mV. When the effluent ORP value was higher than 350 mV, the corresponding COD concentrations were all lower than 30 mg/L, even though DO ranged from 2 to 8 mg/L. This indicated that, at higher ORP values, DO has less influence on ORP than it does at low ORP values. Oxidation–reduction potential values were higher than 350 mV when COD was lower than 30 mg/L. Based on the on-site experimental results, the authors suggest that, to keep effluent COD lower than 50 mg/L and DO higher than 1.0 mg/L, the effluent ORP should be higher than 270 mV.

When both ORP and temperature were taken into consideration, wastewater COD concentrations could be predicted accurately (Figure 4). The predicted effluent COD concentration, based on the following equation that was derived from measured data on-site by multiple regression analysis, is in good agreement with the observed effluent COD (R^2 = 93.43%):

$$\mathrm{COD} = 211.3 - 0.282\ \mathrm{ORP} - 3.776T \qquad (1)$$

To achieve an accurate real-time prediction of water quality, influence factors should be taken into consideration as much as possible, which requires time and labor. The most effective way is to find predominant factors whose differences can be detected when water quality or environmental conditions change. According to Figure 4, ORP and temperature are two factors that can reflect pollutant concentration change. As previously discussed, water temperatures have an effect on the DO concentration in wastewater; as such, temperature can indirectly affect ORP values. By combining ORP with temperature, the aeration tank effluent quality can be predicted accurately.

Muddy Creek Wastewater Treatment Plant. In the Muddy Creek plant aeration tank (HRT = 4.0 hours, aeration throughout the tank), the influent COD was 35 mg/L and the ORP was 421 mV (Figure 5). As at the Mill Creek plant, bulk wastewater ORP values increased with pollutant removal along the length of the aeration

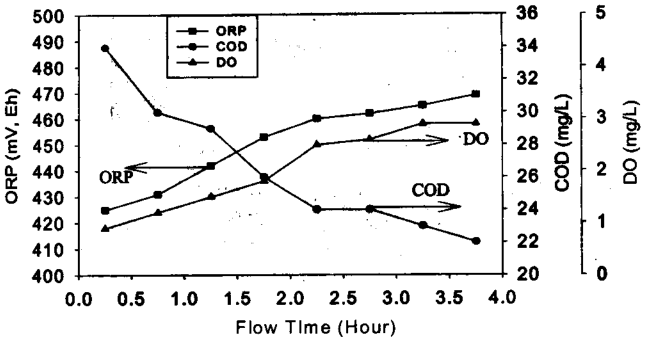

Figure 5—Oxidation–reduction potential, DO, and COD changes along the length of the aeration tank in the Muddy Creek plant (October 26, 2000).

tanks. The DO concentration was 1.0 to 3.0 mg/L along the aeration tank, while effluent COD was 23 mg/L, with an effluent ORP of 472 mV. The mixed-liquor ORP values at the Muddy Creek plant (420 to 472 mV) were higher than at the Mill Creek plant (90 to 370 mV) because of the much lower Muddy Creek wastewater COD.

Wastewater ammonia and nitrate measurements from these two plants showed that minimal nitrification occurred in the Mill Creek aeration tanks (ammonia concentrations in the influent and effluent did not change, with effluent ammonia concentrations still 15 to 24 mg/L and effluent nitrate concentrations of 0.1 to 0.2 m/L), while nitrification did occur in the Muddy Creek plant (the ammonia concentration decreased along the aeration tanks, from 10 to 18 mg/L in the influent to below 1 mg/L in the aeration tank effluent; nitrate increased from 2 to 4 mg/L in the influent to 5 to 15 mg/L in the effluent). Because nitrifiers have a much lower growth rate than heterotrophs, the degree of nitrification often depends on the sludge age, contaminant concentration (Table 1), and oxygen concentration in wastewater. The higher contaminant concentration, use of intermittent aeration, and short sludge age in the Mill Creek plant aeration tanks inhibit the nitrifiers' growth, while the Muddy Creek plant aeration tanks have a suitable environment (low contaminant concentration, constant aeration, and long sludge age) for nitrifier growth. Oxidation–reduction potential values represent the general effect of most biochemical reactions occurring in wastewater. The on-site experimental data show that COD has a prominent effect on ORP values, with ORP ranging from 150 to 380 mV when COD was 20 to 105 mg/L (without nitrification) in the Mill Creek plant aeration tanks; the ORP ranged from 410 to 490 mV when COD was 15 to 35 mg/L (with nitrification) in the Muddy Creek plant aeration tanks. This agrees with previous research indicating that nitrification occurs with ORP values higher than 360 mV (Wareham and Hall, 1993) and different kinds of bacteria dominate at different ORP ranges (Bishop and Yu, 1999). The study suggests that COD oxidation and ammonia oxidation (nitrification) can be distinguished by ORP values of mixed wastewater.

Based on the on-site experiments, it appears that ORP values are affected by several factors such as DO, temperature, and COD. Without sufficient oxygen in the wastewater, biodegradation did not proceed thoroughly and led to low ORP values in the effluent. Among these factors, the mixed-liquor COD stood out as a prominent factor correlating with ORP changes. In the Mill Creek plant, oxygen concentrations change along the length of the aeration tank because of the intermittent aeration system used, although the ORP consistently increased with COD removal in the aeration tanks. Moreover, different ORP values can be used to represent pollutant oxidization (Mill Creek plant) and nitrification (Muddy Creek plant). To use ORP as an online indicator of water quality in aeration tanks, the authors suggest that measuring the ORP values of the effluent is a good option because the extent of biodegradation in the effluent is more complete, leading to more stable ORP readings. The increase in ORP values (the effluent ORP minus the influent ORP) can also be used to indicate the pollutant removal efficiency along the aeration tanks (Li and Bishop, 2001).

There are a number of online indicators used with activated sludge systems (temperature, DO, pH), but none of them can properly indicate the water quality present (i.e., how much contaminant is present in the wastewater) and the treatment efficiency (i.e., how much contaminant has been removed). Compared with these parameters, use of ORP is appealing because it reflects most of the biochemical reactions involved in the wastewater, and has been shown to have a strong correlation with COD concentrations in the aeration tanks. However, it should also be noted that ORP alone is not sufficient for accurately predicting waste quality; to realize optimal online regulation, ORP should be correlated with the temperature, pH, or DO present.

Oxygen Uptake Rate Changes in Aeration Tanks. Oxygen uptake rate is used to indicate the potential for oxygen consumption by microorganisms in mixed liquor. The higher the OUR, the greater the rate at which microorganisms consume oxygen. When aerobic biodegradation is finished, the OUR decreases accordingly. Table 2 shows the OUR changes and pollutant removal along the aeration tanks in the two WWTPs. In the Mill Creek plant, the influent OUR was 3.76 mg DO/L/min, dropping quickly to 1.81 mg/L/min when the air-on zone began after one hour. This means that when the air-on zone began, biodegradation accelerated, leading to a rapid pollutant concentration decrease and a corresponding OUR decrease. Compared with the dramatic OUR decrease in the first part of treatment, the OUR stabilized in the last three hours of treatment. The OUR of the effluent was 1.15 mg/L/min. In the Muddy Creek plant, with its lower wastewater pollutant levels, the OUR was much lower and dropped gradually from 1.20 mg/L/min to 0.57 mg/L/min along the aeration tank. The OUR can affect oxygen transfer in the boundary layer outside activated sludge floc particles and inside the sludge floc. This will be discussed next while considering the microprofile measurements.

Microprofiles of Activated Sludge Flocs. *Activated Sludge from the Mill Creek Plant Aeration Tank.* The diameters of

Table 2—The OUR (mg O_2/L/min) change along the length of the aeration tanks in the Mill Creek and Muddy Creek plants.

Flow time (hour)	0	1.0	2.0	3.0	4.0	5.0	6.0
OUR of Mill Creek plant (mg O_2/L/min)	3.76 ± 0.53	3.42 ± 0.31	2.31 ± 0.42	1.81 ± 0.39	1.53 ± 0.24	1.36 ± 0.25	1.15 ± 0.28
OUR of Muddy Creek plant (mg O_2/L/min)	1.20 ± 0.35	0.97 ± 0.41	0.82 ± 0.31	0.69 ± 0.26	0.57 ± 0.22		

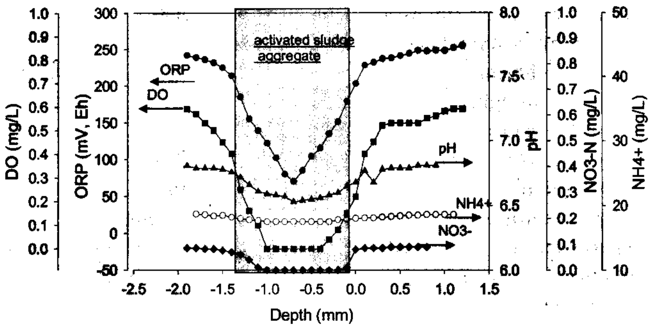

Figure 6—Microprofiles of aeration tank influent activated sludge floc in the Mill Creek plant (October 10, 2000).

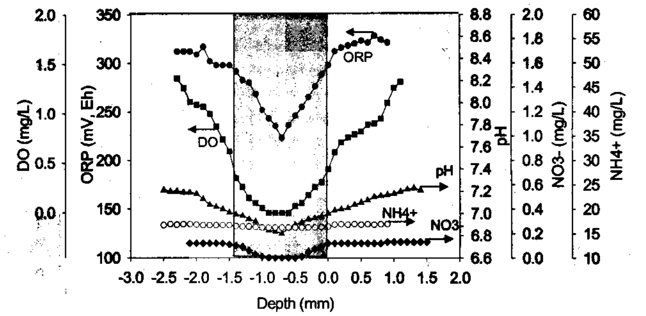

Figure 7—Microprofiles of aeration tank effluent activated sludge floc in the Mill Creek plant (October 10, 2000).

activated sludge aggregates used in this study were 1.0 to 1.4 mm. The microprofiles of ORP, DO, pH, NH_4^+, and NO_3^- as functions of distance from the surface of the activated sludge floc from the aeration tank influent at the Mill Creek plant are plotted in Figure 6. All the data were obtained from a steady-state condition in the floc. The data presented in this paper are not the average values for the floc particles; rather, they represent one typical profile among multiple measurements. Theoretically, when considered as a sphere with uniform mass distribution, the microprofiles inside the activated sludge floc should be symmetrical. However, a few of the experimental profiles were not symmetrical. Possible reasons for this are that (1) an activated floc is a metabolically active entity with numerous biochemical reactions and mass-transfer operations occurring at the same time, which may lead to a nonuniform distribution of mass inside sludge floc; or (2) the floc particle was not strictly spherical or the lower part of floc was compressed by the weight of the upper part of the floc.

The COD in the bulk wastewater from which the floc particle was taken was 123 mg/L, with an ORP value of 246 mV and a DO concentration of 0.58 mg/L (because of the air-off zone in the beginning part of the aeration tank). The oxygen concentration profile seen in Figure 6 demonstrates that DO began to drop quickly at 0.5 to 0.6 mm above the surface of the activated sludge floc (the diffusion zone). Oxygen was depleted in the top 0.2 mm into the influent activated sludge floc particle. The aerobic zone was limited to the top layer of the floc, and the rest of the sludge floc was anoxic. The ORP profile shows that ORP values dropped dramatically, from 246 mV in the bulk water to 68 mV in the sludge center, indicating a significant change in redox status. The reasons for the low ORP values and the sharp depletion of DO inside the floc are the high pollutant concentrations in the wastewater, the high oxygen utilization rate (Table 2), mass-transfer resistances, and DO consumption during the biodegradation of encapsulated pollutants within the floc (Takacs and Fleit, 1995). The pH dropped inside the floc, caused by anoxic reactions. The ammonia concentration in the bulk solution was 17.8 mg/L, with no visible change inside the flocs. The nitrate concentration in the bulk solution was 0.1 mg/L. Nitrate concentrations immediately dropped to zero after penetrating 0.15 mm into the floc, a condition probably caused by denitrification in this zone of low DO concentration. The profile shape clearly shows the heterogeneity of the activated sludge floc, with the exterior part of the floc (upper 0.2 mm) able to fully participate in the metabolism of the pollutants while the anoxic interior of the floc has rapidly decreasing effectiveness.

In profiles of the effluent activated sludge floc from the aeration tank at the Mill Creek plant, where there was a DO of 1.2 mg/L in the bulk water, the anoxic region was limited to only 0.3 mm in the activated sludge floc center (Figure 7). Because of the lower oxygen utilization rate compared to the influent, oxygen penetrated deeper into the aggregate. The COD in the bulk wastewater deceased to 56 mg/L, with an ORP value increasing to 331 mV. The ORP value dropped to 223 mV at the center of the floc. Although ammonia penetrated the sludge, minimal nitrification occurred. The bulk water nitrate concentration was still less than 0.1 mg/L. Based on microelectrode measurements, the sludge floc from the Mill Creek plant aeration tank was rich in substrate but low in oxygen. The oxygen-limiting conditions adversely affected substrate biodegradation.

In a sample taken on another day, when the effluent DO increased to 4.0 mg/L, the oxygen profile demonstrates that oxygen fully penetrated the floc (Figure 8). The DO concentration was 0.56 mg/L in the center region. The ORP decreased from 368 mV in the bulk wastewater to 252 mV in the floc center. The COD of the bulk wastewater decreased to 42 mg/L. With sufficient dissolved oxygen present inside the activated sludge floc, the sorbed particulate substrate was efficiently biodegraded. Accordingly, the ORP value in the core of the floc was higher than at a DO concentration of 1.5 mg/L.

Ammonia concentrations in both the influent and effluent samples remained basically the same inside and outside the activated sludge floc, while all the other parameters (nitrate, pH, ORP, and DO) underwent a decrease inside the floc because of transfer resistance and microbial biodegradation. The ammonia fully penetrated the activated sludge floc because of the minimal nitrification occurring, as evidenced by the bulk wastewater analyses.

Activated Sludge from the Muddy Creek Plant Aeration Tank. The effect of COD concentration in bulk liquor on the ORP and DO

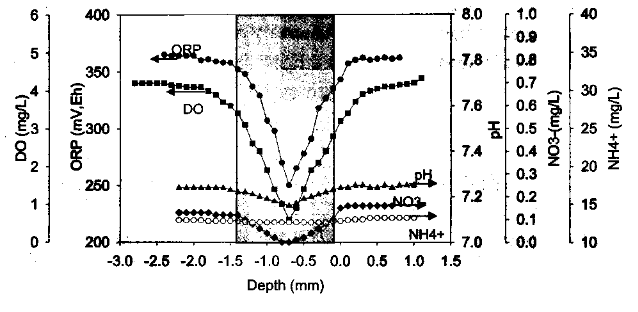

Figure 8—Microprofiles of aeration tank effluent activated sludge floc in the Mill Creek plant when dissolved oxygen is 4 mg/L (October 16, 2000).

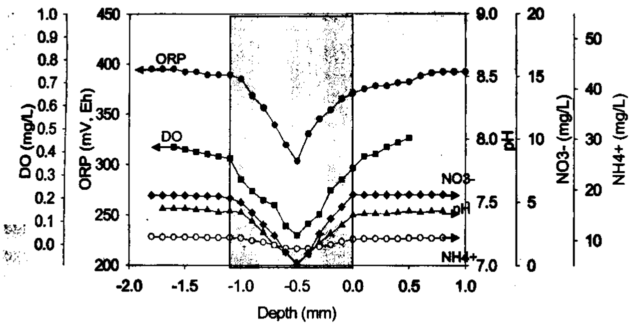

Figure 9—Microprofiles of aeration tank influent activated sludge floc in the Muddy Creek plant (October 16, 2000).

microprofiles of activated sludge can be seen in Figure 9. In the Muddy Creek aeration tank influent, substrate concentration (COD: 34 mg/L) was much lower than in the Mill Creek aeration tank influent (COD: 123 mg/L). While bulk dissolved oxygen was below 0.5 mg/L, dissolved oxygen was zero only in the center of the flocs. The DO decrease rate inside the sludge floc particles was not as dramatic as in the activated sludge floc from the Mill Creek aeration tank. This is the result of the lower OUR (Table 1), which is caused by the lower pollutant concentration in the wastewater. The ORP in the bulk wastewater was 389 mV, which was even higher than in the Mill Creek aeration tank effluent. The ORP was higher than 300 mV in the floc center zone. The rate of pH decease in the aggregate was higher than in the Mill Creek influent because of nitrification occurring in the top layer. The nitrate concentration in the bulk wastewater was 5 mg/L, which decreased inside the activated sludge floc. This is perhaps because of simultaneous nitrification–denitrification (nitrate produced by nitrifiers was quickly consumed by aerobic denitrifiers) or by mass-transfer resistance inside the activated sludge floc.

In the bulk liquid effluent, ORP increased to 428 mV and COD decreased to 21 mg/L (Figure 10). The whole activated sludge aggregate was aerobic. The DO profile shows that DO concentrations decreased slowly within the aggregate. Oxygen decreased from 1.09 mg/L in the bulk wastewater to 0.8 mg/L in the floc center, which indicates the low oxygen utilization rate by the microbial processes. The ORP was 387 mg/L in the floc center. The whole floc particle was aerobic and in a high redox status. Nitrification proceeded well, with a nitrate concentration of 16.5 mg/L and an ammonium concentration of less than 1 mg/L in the effluent.

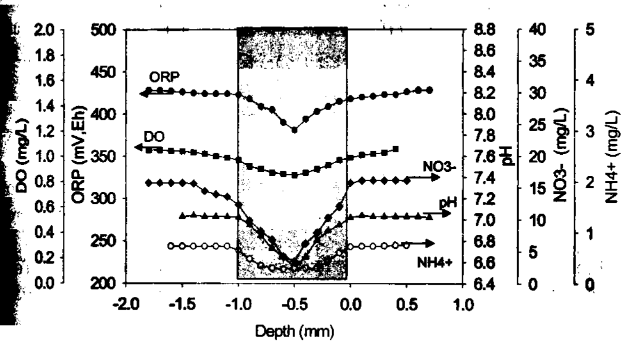

Figure 10—Microprofiles of aeration tank effluent activated sludge floc in the Muddy Creek plant (October 16, 2000).

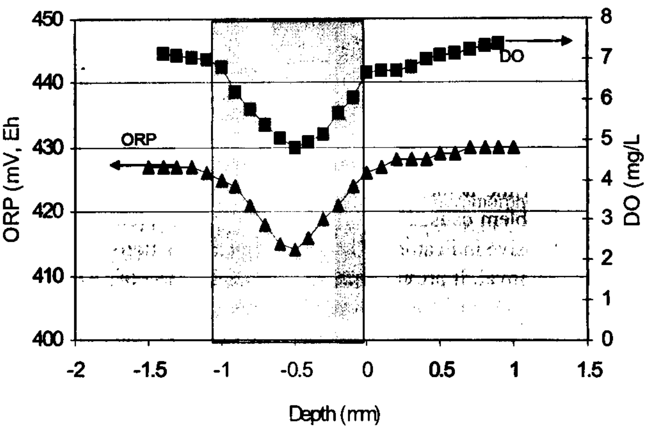

Figure 11—Microprofiles of the activated sludge floc of the Muddy Creek Plant when the dissolved oxygen is 7.6 mg/L.

The microprofiles of activated sludge in fully aerated effluent were also investigated. The COD of the effluent was 18 mg/L, with an ORP of 430 mV. The DO concentration was 7.6 mg/L in the fully aerated bulk wastewater. Figure 11 shows that oxygen penetrated throughout the activated sludge floc and was higher than 5 mg/L, even in the center zone. With a low OUR by the microbial processes, oxygen decreased slowly inside the floc. No further enhancement of the treatment efficiency occurred, compared to a DO concentration of 1.09 mg/L (COD: 21 mg/L). This evidence demonstrates that an aerobic region inside the activated sludge floc is a requirement for good substrate biodegradation by the activated sludge floc (such as in the Mill Creek plant), but excessively high oxygen concentrations are not helpful for increased biodegradation efficiency and may cause unnecessary energy usage.

The average size of the activated sludge floc from Mill Creek Wastewater Treatment Plant was 1.0 to 1.4 mm, while the size of the sludge floc from the Muddy Creek Wastewater Treatment Plant ranged from 0.8 to 1.2 mm. There was no obvious difference in floc size along the length of the aeration tanks at either plant. The floc size is influenced by many factors, such as hydraulic condition, biomass, extra polymeric substances, metabolic byproducts, substrate, and so on (Abbasi et al., 2000). A possible reason for the difference in floc size at the two plants is that, because of the higher contaminant concentration, oxygen could not penetrate as far inside floc from the Mill Creek plant and biodegradation activity was lower, thus causing the accumulation of substrate and metabolic byproduct inside sludge floc. This has been predicted by activated sludge model simulations (Li and Bishop, 2002). To verify this assumption, further analysis of the composition of activated sludge floc needs to be done.

Conclusions

The feasibility of using ORP as a real-time indicator of treatment efficiency and water quality along the length of aeration tanks in the two WWTPs was investigated in this study. The on-site measurement results show that ORP values are strongly correlated with COD removal along the aeration tanks and that DO and temperature also have an effect on redox status improvement and pollutant removal efficiency. The ORP values in aeration tank effluent are suggested for use as an online ORP regulator of aeration tanks. The ORP of the effluent should be higher than 270 to 300 mV for optimum substrate biodegradation and higher than 350 to 400 mV for nitrification.

While substrate removal from the mixed liquor contributes significant ORP increase in the bulk wastewater, microbiodegradation inside the activated sludge floc is necessary for proper substrate stabilization. When combined with other online parameters (temperature, pH, and DO), it is projected that ORP measurement can provide online information concerning water quality and treatment efficiency in the aeration tanks. The ORP regulation resolves the time-lag problem caused by the use of COD measurements, and is a comprehensive indicator of most biochemical reactions involved in pollutant removal. It provides many benefits over use of DO control. The ORP values provide information on water quality (even when oxygen concentrations vary in the bulk wastewater), and thus help to achieve proper real-time aeration adjustments and energy savings.

The effects of substrate and oxygen concentrations on the microprofiles of activated sludge floc from two WWTPs show the heterogeneity of microbial processes inside the floc. With a high microbial OUR in the influent, the aerobic region of the activated sludge floc may be limited to the top layer of the floc particles, as in the Mill Creek plant. The ORP and DO inside the floc increased in parallel with bulk wastewater treatment. When DO in the bulk effluent was higher than 4.0 mg/L, ORP in the activated sludge floc center increased to 250 mV and the anoxic zone inside the floc particle disappeared, which is helpful for biodegradation. With lower pollutant concentrations present in the Muddy Creek plant, the ORP and DO inside the sludge aggregates were higher than those from the Mill Creek plant. The ORP in the floc center was always higher than 300 mV, with significant nitrification occurring. Further increasing the DO concentration did not improve treatment efficiency, although the whole activated sludge floc or aggregate was aerobic and had a high redox status. By integrating microprofiles of activated sludge flocs with the ORP and COD in the aeration tank, it is determined that pollutant removal in the wastewater has an effect on microenvironment changes in the activated sludge floc. The improvement of the redox status inside the floc correlates with biodegradation in the bulk wastewater, indicating wastewater ORP is a general value influenced by pollutant levels and oxygen concentration.

The gentle hydraulic conditions used for the microelectrode measurements may have resulted in the floc size observed in this study being slightly larger than those observed in vigorously mixed aeration tanks. This should not have a significant effect on the results or hamper the practical application of using the microprofiles. Reasonable and reproducible ORP, DO, and nitrate concentration trends inside the activated sludge flocs were obtained from multiple measurements in this study. Although the absolute values may change when applied to smaller flocs, the trends should be the same.

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