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RELATION BETWEEN REDOX POTENTIAL AND OXYGEN LEVELS IN ACTIVATED-SLUDGE REACTORS

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ABSTRACT

The importance of dissolved oxygen level in determining the platinum electrode potential in activated sludge has been clearly demonstrated by current-potential curves plotted at different oxygen concentrations.

Tests have been carried out, in the laboratory and in full scale treatment plants, to define the relationship between the platinum electrode potential at equilibrium (Eh) and the dissolved oxygen [O_2] concentration in the activated sludge. These two parameters obey a law of the form $Eh = a + b \log [O_2]$. The measured values of coefficents a and b differ widely to those found from the oxygen reduction reaction in water (a = 0.8 V at pH 7 and b = 15 mV per decade).

Factors a and b mainly depend on the sludge loading, the aeration conditions and the sludge concentration. Using non-polished stationary platinum ring electrodes, the following values of a were obtained (at pH between 7 and 7.6) : + 410 mV/NHE for sludge aerated for several hours without feeding, + 265 mV/NHE for over-aerated/low-loaded sludge (Cm = 0.2 kg BOD.kg $MLVSS^{-1}$. day^{-1}) and + 180 mV/NHE for high-loaded activated sludge in plug-flow system (Cm = 1 kg BOD.kg $MLVSS^{-1}$ .day^{-1}). Factor b would seem to lie between 55 and 65 mV when the sludge is continuously aerated without feeding. At low loads with excess aeration, it lies between 70 and 90 mV. When the medium is slightly septic at low dissolved oxygen concentrations (insufficient daily aeration time, high sludge concentration or aerators shut down for too long periods), factor b increases and can reach 200 mV. In the same way, at high loads, factor b can become 150 mV.

These results demonstrate the importance of dissolved oxygen concentration in the mechanisms which determine the metal electrode potentials in activated sludge. They also illustrate the role that other electroactive species play in the process. The type and concentration of these species depend on parameters such as the sludge loading, the overall oxygen supply, the aeration sequence and the sludge concentration.

KEYWORDS : activated sludge, redox potential, oxygen, wastewater treatment plant, instrumentation, control.

INTRODUCTION

Various authors have recently demonstrated the practical importance of zero-current potential measurements in activated sludge in controlling nitrification and denitrification processes (Tanaka et al., 1982, Fujii, 1983, Charpentier et al., 1987). Several patents have been taken out as a result of these studies (Hitachi Ltd, Kankyo Engineering Co Ltd, Meidensha Electric Mfg Co Ltd, Mitsubishi Heavy Industries, Nippon Steel Corp.)

The metal electrode potential in aerated sludge probably originates from several sources : redox species in the interstitial water (from the wastewater or produced by the bacterial metabolism), redox enzymes (for example, flavins), pH, dissolved oxygen, etc. The easiest parameters to monitor in treatment plants are the pH and the dissolved oxygen content. Variations in the pH of activated sludge in extended aeration rarely exceed a few tenths of a unit. However, it would seem advisable to measure pH in conjunction with the potential measurements to attempt to determine the reaction mechanisms occurring at metal interfaces.

In general terms, dissolved oxygen is reduced in line with the equation :

$$O_2 + 4\ H^+ + 4\ e^- \rightleftharpoons 2\ H_2O$$

If the partial oxygen pressure is expressed in atmospheres, its normal potential at 20°C is 1.228 V/NHE (Milazzo, 1969). If the dissolved oxygen content is expressed by weight, the normal potential becomes 1.251 V/NHE and the apparent normal potential at pH 7 is then 0.846 V/NHE.

The Nernst equation can then be written :

$$E = 1.251 - 0.058\ pH + 0.015 \log [O_2] \qquad (1)$$

Where :

E : the oxidation reduction potential/NHE (Volts)
log : the logarithm to a base of 10
$[O_2]$: the dissolved oxygen concentration ($mg.l^{-1}$).

Our earlier work on pilot plants demonstrated that, when they are subjected to cyclic feed and aeration conditions, the redox potential of polished platinum electrodes reached at the end of the aeration periods (Eh*) is related to the nitrification efficiency (Heduit et al., 1987_a). The (Eh*) potential for one of the two pilot plants was found to be closely correlated with the dissolved oxygen concentration

$$Eh^* = 0.398 + 0.080 \log [O_2] \qquad n = 6 \qquad r = 0.92. \qquad (2)$$

This equation is similar to (1) :

$$E = a + b \log [O_2]$$

but parameters a and b differ significantly from thermodynamic values.

Regardless of variations due to the dissolved oxygen concentration, the electrode potential in activated sludge seems to be heavily affected by other electroactive species : according to Nussberger, quoted by Burbank (1982) and Bejaoui (1977), the potential reached by a platinum electrode in sludge sampled from a plant and then aerated without feeding is higher if the plant is underloaded or over-aerated.

Finally, it must be remembered that the metal electrode potential at equilibrium conditions in activated sludge is not an equilibrium thermodynamic potential since low-concentration electroactive species are probably involved. This means that the surface condition of the electrode (and, therefore, the preparatory treatment applied to it) has a considerable effect on its response (Coquery, 1986 ; Heduit et al., 1987_b). However, it is possible to obtain repeatable measurements (to within $\pm$ 10 mV) at stabilized conditions by using electrodes in the same material, of the same shape and prepared in the same way.

MATERIAL AND METHODS

1. ELECTROCHEMICAL EQUIPMENT

In the laboratory, the current-potential curves were plotted at low speed ($1.25\ mV.s^{-1}$) using a Tacussel PRG 3 assembly comprising :

- a potential controlling unit (PRT 20-2X)
- an adaptor unit (UAP 3)
- a voltage recorder (EPL 2) fitted with a control system.

The plots were taken from fixed platinum electrodes dipped into stirred samples. The indicating electrodes, used both for laboratory and on-site tests, consist of a platinum ring (S = 0.5 cm^2) (Ingold Pt 805). The reference electrodes (Xerolyt) contain a solid electrolyte. On the site, they are placed in PVC tubes fitted with O-rings which allow them to be submerged to approximately 80 cm. The indicating electrodes and the common reference electrode used with them are connected to high input-impedance millivoltmeters (Knick 646), themselves connected to graphic recorders (Goerz Servogor 460.06) fitted with variable sensitivity units. Ponselle O_2P oxygen-meters (amperometric sensors) are used to measure the oxygen concentrations. Portable Schott CG 817 pH meters are used.

2. THE LABORATORY TEST CELL

This is a rectangular 2 liter transparent PVC cell capable of accommodating 10 electrodes. It is generally placed on a magnetic agitator and the liquid is stirred by a teflon rod. The dissolved oxygen concentration in the medium is varied by an aquarium compressor or a bottle of nitrogen.

3. WASTEWATER TREATMENT PLANTS

Tests were carried out on 3 different plants.

The Crisolles (Oise) plant has a nominal capacity of 40 kg BOD.day^{-1} and the Fontenay-Tresigny (Seine et Marne) plant 300 kg BOD.day^{-1}. Both operate on activated sludge/extended aeration/complete mixing mode. They are equipped with intermittently-operating surface aerators : At Crisolles, it is a 7.5 kW SEM low-speed vertical-axis aerator on a cylindrical aeration tank (V = 140 m^3) and at Fontenay-Tresigny, two 15 kW France Assainisement/Rollox low-speed horizontal-axis aerators on an annular basin (V = 1040 m^3).

The Colombes (Hauts de Seine) aeration basin tested (V = 800 m^3) operates at high loads (1 kg BOD.m^{-3}.day^{-1}) and on plug flow. It is fitted with a fine air bubble blowing system, controlled by an oxygen-meter, and receives decanted wastewater.

The flows were measured using an Isco bubble flow-meter (with record and printer), coupled to the plant weir. The inlet and outlet water samples are collected by APAE 241 F and ISCO automatic samplers respectively. Table 1 summarizes the main operating parameters of these plants during the experimental period.

Table 1 : Process operating parameters for the 3 plants tested

Treatment Plant	C_m°	C_v°°	MLSS* % MLVSS**	HRTxxx	Daily aeration time	pH	θ (°C)	Results of effluent analysis ($mg.l^{-1}$)			
								DCO	$N\text{-}NH_4^+$	$N\text{-}NO_2^-$	$N\text{-}NO_3^-$
Crisolles Aug.17-20(87)	0.2	0.3	2.6 60 %	26	10 h	7.5- 7.6	21°	35	3	0.4	7
Fontenay-Tresigny Aug. 6-11 (1987)	0.04	0.2	8.5 65 %	35	10 h 45	7.2- 7.4	18°	20	0.7	0.02	0.2
Aug.31- Sep.3 (1987)	0.04	0.2	8.1 67 %	35	8 h 45	7 - 7.2	18°	50	4.5	0.04	0.3
Colombes Aug.25-27(87)	1.2	1.05	1.3 67 %	1 h 20	continu	7 - 7.5	18°	40	5	0.3	2

°C_m : sludge loading (kg BOD.kg MLVSS^{-1}.day^{-1})
°°C_v : BOD loading (kg BOD.m^{-3}.day^{-1})
* MLSS : mixed liquor suspended solids ($g.l^{-1}$)
% MLVSS : percentage of mixed liquor volatile suspended solids in the MLSS (%)
HRTxxx : Hydraulic Retention Time (h).

4. ELECTROCHEMICAL MEASUREMENT

In the presence of a reversible equilibrium between species such as $[Fe(CN_6)]^{3-}/[Fe(CN_6)]^{4-}$ which rapidly exchange electrons with the electrode and if their concentration is sufficiently high, an inert electrode reaches a reproducible equilibrium potential ($E_{I=0}$) defined by the Nernst law. In these conditions, the electrode is subjected to two opposite-polarity currents (Jo_a and Jo_c) such that the resultant current is zero (figure 1).

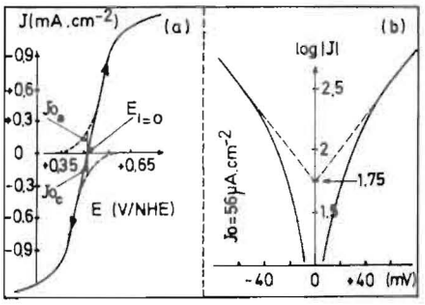


Fig. 1 : (a) Voltammetric recordings and (b) TAFEL plots for the system 0.5 mM $[Fe(CN)_6]^{4-}$ /0.5 mM $[Fe(CN)_6]^{3-}$ in KOH 1 M - rotating disk electrode (3000 r.p.m.) - platinum disk surface area : 0.03 cm^{-2} - potential scan rate : 100 $mV.min^{-1}$

To measure the zero current potential, it is first necessary to determine the difference between the metal electrode equilibrium voltage and the potential of a reference electrode. This is done using a high input-impedance millivoltmeter.

The equilibrium current density (Jo) is conventionally determined, at pure transfer conditions, by recording current-voltage curves at anodic or cathodic potential scans low speeds (voltammetric measurement) and then plotting curves of the logarithm of the current density (log J) against the applied overpotential (η). The exchange current density (Jo) at the equilibrium potential is then determined by extrapolating these curves to zero overpotential :

$$\log |J| = \log |Jo| + K\eta$$

where :

J : the current density = (current through the circuit/working electrode area ($mA.cm^{-2}$)
Jo: the exchange current density ($\mu A.cm^{-2}$)
η : the overpotential = applied potential imposed - equilibrium potential (V)

5. LABORATORY AND ON-SITE TEST PROCEDURES

In the laboratory, the electrodes are cleaned and then dipped into the medium approximately one hour before starting measurement. To clean the platinum electrodes, they are simply washed in tap water after degreasing them with acetone. The sludge is always aerated before submergence of the electrodes and the first values measured are always those at the highest value of the variable oxygen concentration [O_2]. In this case, each oxygen concentration and potential equilibrium point is held for at least 10 minutes. The preparatory treatment may be repeated during the experiments to check the repeatability of the measurement at a given oxygen concentration.

On the site, several platinum electrodes, the common reference electrode and an O_2 sensor are introduced into the aeration tank simultaneously. Flow measurements and water sampling begin at the same time. The hourly samples taken are grouped in proportion to the corresponding flow to form 24 hours composite samples which are then analyzed for COD and ammonia, nitrous and nitric nitrogen. The temperature, pH, mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) are measured on the sludge each day. The electrodes are cleaned each day and each test period lasts three to six days.

All zero current potential (Eh) values have been averaged for 2-3 indicating electrodes.

RESULTS AND DISCUSSION

1. VOLTAMMETRIC MEASUREMENT

Figure 2 gives the typical current-potential curves obtained from platinum electrodes in activated sludge at three different dissolved oxygen concentrations. The progressive disappearance of the cathodic branch as the dissolved oxygen concentration diminishes shows that this branch probably represents the electrochemical reduction of the dissolved oxygen.

These experiments show how the dissolved oxygen reduction reaction contributes to the establishment of a metal electrode equilibrium potential in activated sludge. Tafel plots obtained for figure 2 experimental conditions give an equilibrium exchange current density around 40 nA.cm^{-2} (anodic and cathodic scans).

The following values had already been measured for this type of electrode under steady state conditions (Heduit, 1985) :

. 20 nA.cm^{-2} in sludge held under anoxic conditions (E = - 0.3 V/NHE)

. 50 nA.cm^{-2} in aerated activated sludge under endogenic uptake rate (E = + 0.3 V/NHE) and 24 hours after electrochemical pretreatment of the metal (triangular signals at 2500 Hz between - 1.5 and + 1.5 V/SCE for 2.5 minutes).

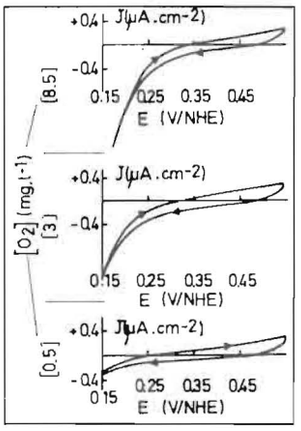


Fig. 2 : Voltammetric curves at different dissolved oxygen levels in activated sludge stationary electrode - platinum surface area : 0.5 cm^{-2} - scan rate : 75 mV.min^{-1}

These very low density values for the exchange current Jo are related to the electrochemical species present in the medium (slow systems) and the fact that the metal is not activated. Densities 10 times higher were found immediately after mechanical polishing of the metal. However, this effect disappears within a few hours (Heduit, 1985). This type of treatment cannot be easily automated on a real site and so was not used during the remainder of the experiments described here.

2. RELATION BETWEEN ZERO-CURRENT ELECTRODE POTENTIAL AND DISSOLVED OXYGEN CONCENTRATION

2.1. Effect of preliminary aeration of sludge

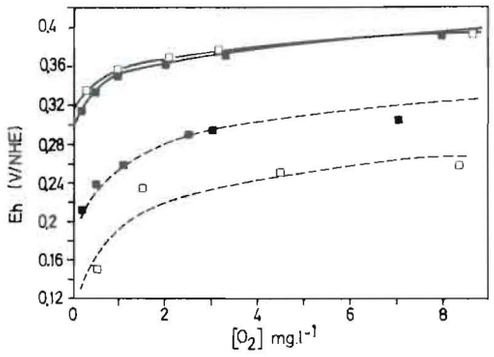


Fig. 3 : Variation of zero-current potential with dissolved oxygen concentration in activated sludge, sampled from the Fontenay-Tresigny plant, :
(___) sludge previously aerated for 12 hours without feeding
(---) sludge previously held under anoxic conditions for 12 hours without feeding
□ First experimental period
■ Second experimental period

Figure 3 shows the variations, obtained in the laboratory, of the zero current electrode potential (Eh) plotted against the dissolved oxygen content [O_2] in activated sludge which was previously either aerated, without feeding, for 12 hours or held under anoxic conditions, without feeding, for the same period. These sludges were sampled from the Fontenay-Tresigny treatment plant during 2 different periods described in Table 1.

The effect of pH on the results must be mentioned : over-aeration of the sludge immediately prior to the experiment causes an appreciable increase in pH (from 7.2 to approx 8.5) due to displacement of the CO_2. The reverse is also true, i.e. the pH is reduced by approx 0.5 unit when the dissolved oxygen concentration is reduced during the experiment.

Sulfuric acid and then soda were added to treated water, saturated with dissolved oxygen at 21°C, to assess the effect of variations in pH on the Eh potential (see Figure 4).

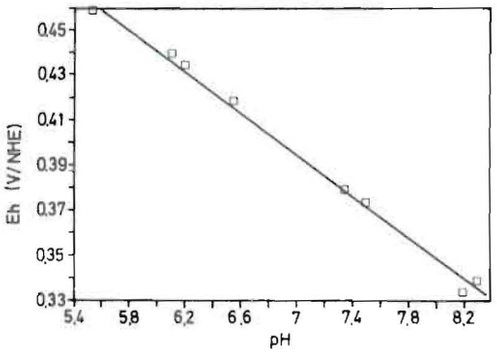


Fig. 4 : The effect of pH on the Eh of treated water from the Fontenay-Tresigny plant (the sample was lightly acidified by adding H_2SO_4 then alkalized by NaOH)

The following relationship has been obtained :

$$Eh = 0.721 - 0.046\ pH \qquad (n = 8\ ;\ r = 0.99) \qquad (3)$$

Using this 46 mV variation of Eh per pH unit, figure 3 data were corrected to "standardize" them at pH = 7. These corrected values were plotted against log [O_2] (figure 5). The linear regressions obtained from these corrected values give :

$$Eh_7 = 0.407 + 0.055 \log [O_2] \qquad (n = 5\ ;\ r = 0.95) \qquad (4)$$
(1st experimental period, 12 hours preliminary aeration)

$$Eh_7 = 0.412 + 0.060 \log [O_2] \qquad (n = 6\ ;\ r = 0.99) \qquad (5)$$
(2nd experimental period, 12 hours preliminary aeration)

$$Eh_7 = 0.220 + 0.089 \log [O_2] \qquad (n = 4\ ;\ r = 0.92) \qquad (6)$$
(1st experimental period, 12 hours anoxia)

$$Eh_7 = 0.321 + 0.077 \log [O_2] \qquad (n = 6\ ;\ r = 0.99) \qquad (7)$$
(2nd experimental period, 12 hours anoxia)

Eh_7 = electrode potential corrected back to pH = 7 (V/NHE)

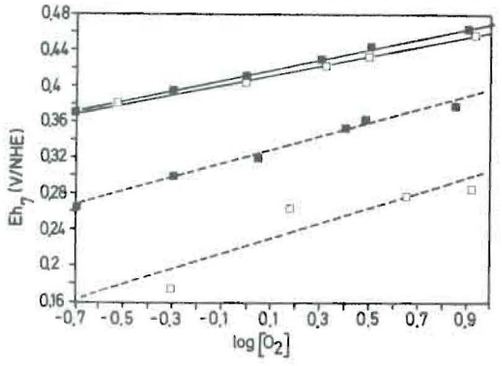


Fig. 5 : Eh potential values from figure 3 corrected back to pH = 7 (46 mV shift per pH unit) against the logarithm of the corresponding dissolved oxygen concentration (expressed in mg $O_2.l^{-1}$)
(___) sludge previously aerated for 12 hours without feeding
(---) sludge previously held under anoxic conditions for 12 hours without feeding
□ First experimental period
■ Second experimental period

The two continuous lines (sludge previously aerated for 12 hours) are very close to each other. Both dotted lines (sludge held under anoxic conditions for 12 hours) are lower than continuous lines and separated from each other (figure 5). This discrepancy between the dotted lines related to the difference in the length of the aeration period prior to the experiment. If a sufficient aeration period is used, these two dotted lines rise and coincide with the continuous lines. This experience shows that, depending on the sludge aeration conditions, the absolute value of the potential measured varies significantly at a given oxygen concentration.

2.2. The effect of sewage addition

Adding 20 ml of wastewater into 2 liters of aerated sludge causes an immediate drop in the sludge potential by 20 to 50 mV. The dissolved oxygen concentration drops by a maximum of 1 mg/l (from 8 to 7 mg/l) but the pH remains constant (figure 6). After several minutes, the potential and oxygen concentrations return to their initial values. Under these conditions, the potential drop seems directly related to wastewater species or to biological products, indeed oxygen level would not modify Eh by more than 3 mV (see figure 3).

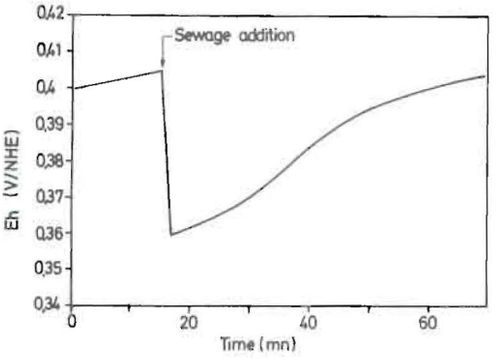


Fig. 6 : The typical effect of adding 20 ml of waste water to 2 liters of activated sludge from the Fontenay-Tresigny plant previously aerated for 12 hours without feeding

2.3 Data collected from real plants

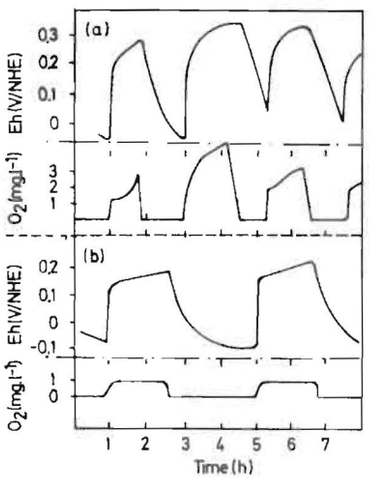


Fig. 7 : Examples of corresponding changes in Eh potential and dissolved oxygen concentration in an intermittently aerated basin (Fontenay-Tresigny plant)
a : first experimental period
b : second experimental period

The evolution of Eh and dissolved oxygen curves obtained from wastewater treatment plants fitted with surface aerators present 2 alternative patterns :

Either both the dissolved oxygen concentration and the potential rise instantaneously as the aerator starts and then tend to become asymptotic (figure 7 a) or, when the aeration is started, the oxygen concentration and potential again rise immediately but the oxygen concentration quickly stabilizes at a relatively low value while the potential continues to increase slowly (figure 7 b).

In the first case, the degradation of the substrate (oxidation) quickly depletes the nutritive substance in the medium and thus reduces the oxygen uptake rate, causing an attendant increase in dissolved oxygen concentration and potential. In the second case, the fact that the oxygen concentration quickly stabilizes at a low value leads to constant high oxygen uptake rate (excessive substrate). As aeration continues, the organic matter is assimilated or oxidized and the potential, therefore, continues to increase. In neither case are the potentials completely stable. They are not, therefore, truly equilibrium potentials even after aeration for several hours.

The potentials reached at the end of the aeration periods were plotted against the logarithm of the dissolved oxygen concentration for the Crisolles treatment plant (figure 8).

The equation of the regression line is :

$Eh^* = 0.264 + 0.091 \log [O_2]$ (pH = 7.5 ; r = 0.92 n = 37) (8)

where :

Eh^* = potential reached at the end of the aeration period (V/NHE)

$[O_2]$ = the dissolved oxygen concentration ($mg.l^{-1}$)

At a given dissolved oxygen concentration, the potentials measured *in situ* are considerably lower than those obtained in the laboratory when sludge samples are aerated without feeding (see figure 5).

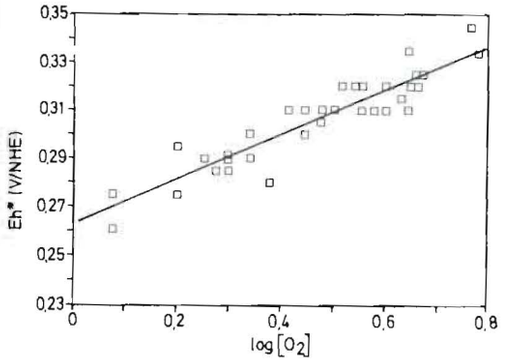


Fig. 8 : The Crisolles plant : potentials reached *in situ* at the end of the aeration periods against the logarithm of the dissolved oxygen concentration (expressed in mg $O_2.l^{-1}$)

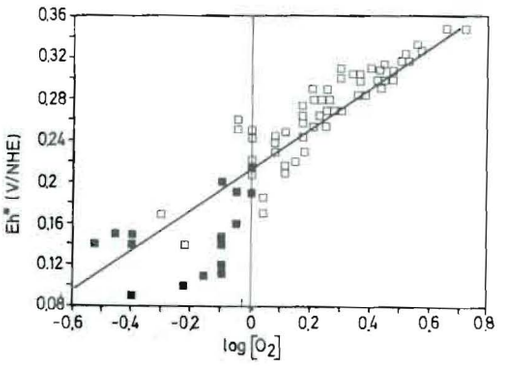


Fig. 9 : The Fontenay-Tresigny plant : potentials reached *in situ* at the end of the aeration periods against the logarithm of dissolved oxygen concentration (expressed in mg $O_2.l^{-1}$).

The potentials achieved at the end of the aeration periods have been plotted against the logarithm of the dissolved oxygen concentrations for the Fontenay-Tresigny treatment plant (figure 9). The equation of the regression line is :

$Eh^* = 0.213 + 0.197 \log [O_2]$ (pH = 7.2 ; r = 0.90 ; n = 96) (9)

The points are widely dispersed around the average line for the lowest oxygen concentrations.

Although the quality of the treated water decreased from one experimental period to the other, due to a reduction in the aeration time after the first period (see table 1), the initial equation (10) is only slightly modified if the 32 points from the second experience are considered ($Eh^* = 0.223 + 0.191 \log [O2]$ (n = 64 ; r = 0.91) (10).

On the other hand, both the potentials and the dissolved oxygen concentrations at the end of the aeration cycle drop when the water quality drops.

At Colombes, the oxygen concentrations and potentials were stabilized at 5.6, 2 and 0.2 mg $O_2.l^{-1}$ for several hours. The regression equation obtained by plotting the corrresponding potentials against the logarithm of the dissolved oxygen concentrations for these values is :

$Eh = 0.180 + 0.148 \log [O_2]$ (r = 0,99 ; n = 3) (11)

3. DISCUSSION

Figure 10 shows all the linear regressions obtained from potential and dissolved oxygen concentration measurements taken at Crisolles, Fontenay-Tresigny and Colombes (see figures 8 and 9 and equation 11). They also show the regression line representing the average of the two sets of measurements taken, in the laboratory, on Fontenay-Tresigny sludge aerated for 12 hours without feeding (see figure 5) :.this line is the highest on figure 10 and its slope is 58 mV per decade. The laboratory finding that adding substrate to sludge causes a drop in potential which is independent of the oxygen level is confirmed by the respective position of all these lines. The regression line obtained on Crisolles plant lies considerably below the previous one and has a steeper slope (91 mV per decade). This indicates that the effect of the dissolved oxygen concentration on the overall redox situation in the medium is far higher than in the previous case.

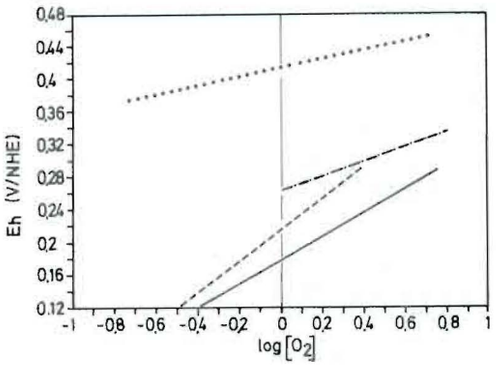


Fig.10 : Comparison between the regression lines obtained by plotting electrode potential in activated sludge versus log $[O_2]$
(....) laboratory samples from Fontenay-Tresigny when subjected to endogenic uptake rate.
(-.-.) *in situ* Crisolles site,
(----) *in situ* Fontenay-Tresigny site,
(____) *in situ* Colombes site.

Like Crisolles plant, the Fontenay-Tresigny plant is very lightly loaded but the calculated regression line is below that for Crisolles (the medium is more strongly reductive) and its slope is 197 mV per decade (the dissolved oxygen concentration strongly affects the interstitial liquid redox situation). The position of this line, and its slope, can be explained by a probable evolution of the highly-concentrated sludge (see table 1) into strong anaerobic conditions in the settling tank and during the aerator shut-down periods (see figures 3 and 5); a second factor is the low dissolved oxygen concentrations pertaining at the end of the aeration periods. Finally, for the Colombes plant which operates at high sludge loading, the factor of proportionality between Eh and the logarithm of the dissolved oxygen concentration is high ; at the same dissolved oxygen concentration, the potentials are always lower than those found in the other stations tested.

CONCLUSIONS

The electrochemical balance involving the dissolved oxygen plays a major role in establishing the equilibrium potential in activated sludge. The electrode potential at equilibrium (Eh) and the dissolved oxygen concentration $[O_2]$ obey a law of the type $Eh = a + b \log [O_2]$ (see figure 10). These experiments clearly show that the value of factors a and b are considerably different from those calculated theoretically from the dissolved oxygen reduction reaction - see equation 1 (0.8 V/EHN and 15 mV/decade). This reaction does not, therefore, determine the equilibrium potential in activated sludge. Although the equilibrium potential and the dissolved oxygen concentration are closely linked, they are not "equivalent". The platinum electrode potential in activated sludge is affected by other electroactive species in the interstitial water whose nature and concentration are mainly determined by the load, the overall oxygen input, the aeration sequence and the sludge concentration.

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