MECHANISMS AND KINETICS OF COD REMOVAL AND SIMULTANEOUS OXYGEN CONSUMPTION IN A ROTATING BIOLOGICAL CONTACTOR BIOFILM

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ABSTRACT

A study on aerobic biofilm COD removal and simultaneous respiration is made using a Wazu respirationmeter unit. In a closed recirculating system completely submerged RBC biofilm samples have been examined in short-term batch experiments, using the corresponding waste water or dissolved acetate. The removal of dissolved organic substrate and the respiration were found to answer the \( t \)-order/0-order kinetic model, whereas the removal of suspended solids COD (CODs) showed 1-order kinetics. Under conditions usually met in practice the 0-order rates for dissolved COD (CODd) removal and respiration were 30-40 gm\(^{-2}\)d\(^{-1}\) and 10-16 gm\(^{-2}\)d\(^{-1}\), respectively; in absence of organic substrate a certain background respiration was observed (3.5-9.0 gm\(^{-2}\)d\(^{-1}\)). As a result of the 1-order kinetics over a wide concentration range, extremely high CODs removal rates were observed even exceeding 300 gm\(^{-2}\)d\(^{-1}\). The difference between the maximum respiration and the CODs removal rates is attributed to physical biofilm adsorption processes. Biofilm COD removal kinetics for waste water containing both CODs and CODd are discussed, illustrating that the kinetic order of the combined process and the reaction constant strongly depends on the CODs/CODd ratio. Conclusion is that a RBC biofilm loaded with a CODs/CODd mixture oxidizes some dissolved organic matter and acts as a catalyst in the coagulation and flocculation of fine suspended solids.

KEYWORDS

COD removal, respiration, biofilm reaction kinetics, biological waste water treatment, fixed-biofilm reactor.

INTRODUCTION

Fixed-biofilm reactors are widely used as treatment systems for liquid organic wastes originating from industrial as well as domestic sources. The most common application is secondary treatment after sedimentation. A relatively new application is upgrading aerobic secondary effluents by means of rotating biological contactors (RBC) (Marsh et al., 1981; Poon et al., 1981a, b). Since anaerobic treatment processes are also successfully applied as pretreatment even to low strength waste water (Lettinga et al., 1983), post-treatment of anaerobic effluents may become another important issue in waste water treatment in order to meet the restrictions set for discharge of effluents. Bovendeur and Klapwijk (1986) showed that this goal too could be achieved using the aerobic fixed-biofilm process, supporting the benefits of the anaerobic pretreatment, viz. low energy requirement.
However, for all possible applications there is a need for information on process mechanisms and kinetics enabling a rational design and operation. As a result many empirical formulas have been proposed, of which Roberts (1973) could list more than a dozen in the field of trickling filtration for a 40 year period. On the other hand, more recently also conceptual biofilm models have been introduced, mathematically associating diffusional transport of dissolved substrates, and the active biofilm thickness with specific reaction kinetics (Williamson and McCarty, 1976a, b; La Motta, 1976a, b; Famularo et al., 1978; Harremoës, 1978). It was shown that the biofilm reaction rate per unit area could be described by first-order, half-order, and zero-order kinetics in relation to the bulk substrate concentration.

These models, however, deal with the removal kinetics for soluble substrates only, whereas most waste waters in practice contain significant amounts of suspended substrate solids. Previous research on RBC performance treating anaerobically digested sewage (Bovendeur and Klapwijk, 1986) showed either total organic removal rates directly proportional to the loading rate, even at extremely high loadings, or a constant removal rate was found independent of the loading rate. This phenomenon could be explained by taking into account the suspended solids content of the feed: high suspended solids contents corresponded with the proportional removal rates and loading independent removal rates were found for low contents of suspended solids. This was confirmed by examining the relationship between removal and loading rates based on filtrated water samples. Similar results were reported by Rusten (1984) for aerated submerged filters loaded with presettled waste water, where the relation between total organic removal rate and organic load was modelled with a hyperbolic function having a very slight curve.

Moreover, there are strong indications by the work of Särner (1980, 1986) that the removal of particulate and dissolved organics interact in the sense that particle adsorption on biofilm surfaces decreases the removal rate of dissolved organics.

The present study is a contribution to the discussion on the mechanisms and kinetics of organic matter removal in fixed-biofilm reactors by combining RBC kinetics for organic matter elimination processes with the simultaneous respiration, and substrate concentrations in the bulk liquid. Emphasis is put on the application of RBC for post-treatment of anaerobic effluents.

**MATERIALS AND METHODS**

**Rotating biological contactor units**

Two identical laboratory-scale RBC units were used. Each unit consisted of 10 disks of expanded polystyrene (disk diameter 0.20 m; thickness 0.01 m; disk spacing 0.02 m) providing a total effective biofilm surface of 0.69 m², of which 50% was continuously submerged. The disks were mounted on a horizontal steel shaft, rotating in a triangular trough (total effective liquid volume 0.066 m³). The rotational speed of the disks was 25 rpm, resulting in a peripheral velocity of 0.26 ms⁻¹.

**Biofilm growing conditions**

Non-nitrifying RBC biofilm material was obtained by continuous loading the two RBC units with two types of waste water (hydraulic loading rate 0.21 m³m⁻²d⁻¹, hydraulic residence time 1 h). One RBC unit was loaded with raw domestic sewage, anaerobically digested in a 6 m³ UASB reactor (Upflow Anaerobic Sludge Blanket) described in detail by Grin et al. (1983) and De Man et al. (1986). The resulting biofilm sample is denoted as "UASB effluent biofilm". The second RBC unit was loaded directly with the presettled domestic sewage, thus producing a "domestic sewage biofilm" sample. Basic loading conditions varied between 60 and 90 gm⁻²d⁻¹ total COD (Chemical Oxygen Demand), depending on the strength of the incoming sewage (combined sewer system). The ambient temperature of the sewage and the UASB effluent as well varied between 12 and 20°C. After reaching a relatively constant COD removal performance, the biofilm samples were alternately used for experiments in the biofilm monitoring system.
Biofilm monitoring system

The biofilm monitoring system is composed of a biofilm reactor unit (total effective liquid volume 0.025 m³) connected to a respiration meter unit (Fig. 1). Dissolved oxygen levels in the reactor unit were controlled by supply of air in the aerator. The water recycle flow between reactor vessel and aerator was set at 0.25 m³h⁻¹ and checked daily. A complete set of disks including the shaft was taken out of the trough of the RBC units and placed vertically in the reactor vessel. At the start of an experiment the reactor vessel is closed without enclosure of air. The attached RBC biofilm sample is examined batch-wise in the system, the disks being completely submerged and rotating at 25 rpm, during several hours at a constant temperature, set by the ambient temperature of the waste water. The RBC biofilm COD removal rate is determined from water samples taken at certain time intervals (0.25, 0.50, or 1.0 h), and analysed for COD.

The overall oxygen consumption by the biofilm sample, denoted as respiration, is monitored by the respiration meter unit (Fig. 1). Dissolved oxygen is measured periodically in the inflow and outflow of the reactor vessel using only one oxygen sensor. This procedure is realised by alternately changing the flow direction in the connecting bypass using a reversible pump. The oxygen sensor is connected to a modular microprocessor system, calculating the respiration rate and controlling the reversible pump. Complete respiration measurements are executed every 4 minutes. The respiration meter unit used (Wazu respiration meter, patent pending), and its operation and possibilities are described in more detail by Klapwijk et al. (1987), and Spanjers and Klapwijk (1987). The biofilm respiration is obtained by correcting the measured respiration for the oxygen consumption by the waste water itself (determined in the biofilm monitoring system in absence of a biofilm sample). The disks including the attached biofilm sample are replaced in the original RBC unit immediately after termination of the experiment, and left there for adaptation during several days, before a new test is performed. Before each test the walls of the complete monitoring system are cleaned, disinfected, and rinsed with tap water. The amount of oxygen involved with COD removal, i.e. COD oxidation, is determined by combining the respiration data and the COD removal data. The biofilm rates for COD removal and respiration are expressed as gm⁻²d⁻¹.

![Schematic presentation of the biofilm monitoring system](https://iwaponline.com/wst/article-pdf/22/1-2/75/100746/75.pdf)
Experimental set-up

The COD removal performance of the biofilm samples has been examined in the RBC units under batch loading conditions by grab samples of the RBC feed and RBC effluent over a 1 h period.

Batch-wise biofilm monitoring experiments were performed loading the RBC biofilm sample with the corresponding type of waste water. The UASB effluent biofilm sample has also been loaded with dissolved sodium acetate as a model substrate for verification purposes of both the biofilm monitoring system and dissolved organic substrate removal performance. In some experiments extremely high suspended solids contents of the UASB effluent were applied, achieved by shaking the pipes connecting the UASB reactor and the RBC units. The absence of nitrifying micro-organisms in the biofilm samples has been checked regularly.

Analyses

COD was analysed according to Standard Methods (American Public Health Association, 1980). Distinction was made between total COD (COD_t), COD after filtration (COD_f) using Schleiden & Schuell paper filters (fraction < 7.4 μm), and dissolved COD (COD_d) after filtration using Schleiden & Schuell membrane filters (fraction < 0.45 μm). Suspended solids COD (COD_s) was calculated as COD_t-COD_f and colloidal COD (COD_c) as COD_f-COD_d. Acetate was determined by gas chromatography using a Packard Becker Model 427 equipped with a 2 m column and flame ionisation detector. The column was packed with Super Copol Fluorad (100-200 mesh) and the carrier gas used was nitrogen gas.

RESULTS

COD removal performance in batch experiments

The removal rates per unit biofilm area for COD_s, COD_f, and COD_d in UASB effluent are plotted versus the concentration of the corresponding COD fraction (average concentration over 1 h period) in Fig. 2. Distinction is made between measurements in the RBC unit (50% submergence) and measurements in the biofilm monitoring system (100% submergence), showing little - if any - difference. Characteristic distinction was found for COD_s removal performance in comparison to COD_f or COD_d removal performance.

Simultaneous COD removal and respiration performance

Two examples of the output of the biofilm monitoring experiments are given in Fig. 3 and 4. In Fig. 3 the cumulative removal of acetate and the respiration, as well as the respiration rate plotted versus time for the UASB effluent biofilm sample fed with acetate. The total respiration followed the course of the acetate removal, indicating that acetate removal is mainly the result of a biochemical process including acetate oxidation. The respiration rate reached a more or less constant high level during about 4 hours, starting almost immediately after initiating the experiment. After this period the respiration rate decreased strongly until a certain background respiration rate was reached. Fig. 4 shows the same relations for the UASB effluent biofilm sample fed with the corresponding effluent. In contrast to the acetate experiments, a minor effect was observed for the initial increase of the respiration rate on total respiration (Fig. 4a), due to a less rapid increase of the respiration rate after initiating the experiments (Fig. 4b). The background respiration rate was found to be constant over an extended period. The background and maximum levels for the respiration rates observed for the different combinations of biofilm samples and effluents are presented in Table 1.
Mechanisms and kinetics of COD removal

Effect of substrate concentration

The relation between the dissolved organic substrate removal rate and the respiration rate on one hand, and the bulk concentration of both dissolved organic substrate and dissolved oxygen on the other hand, is shown in Fig. 5 for all experiments in which the UASB effluent biofilm is fed with acetate. The combined results demonstrate that both rates reach a more or less constant level (about 20 gm⁻²d⁻¹ acetate; 13 gm⁻²d⁻¹ oxygen), once certain minimum concentrations have been exceeded (about 30 gm⁻³ acetate; 1.6 gm⁻³ oxygen). However, the measurements of the acetate removal rate scatter significantly more than the respiration rate measurements. Biofilm performance in terms of the background respiration rate related to the bulk concentration of dissolved oxygen is shown for a single experiment, again using the UASB effluent biofilm sample (Fig 6). The result suggests that the constant level of the background respiration rate observed in the biofilm monitoring experiments described, appears for dissolved oxygen levels exceeding 1.0 gm⁻³, in absence of organic substrate in the bulk liquid.

TABLE 1. Background and Maximum Levels of the Respiration Rate (r ± SD (n)), measured in two series (a, b) of experiments

<table>
<thead>
<tr>
<th>biofilm sample</th>
<th>UASB effluent biofilm</th>
<th>domestic sewage biofilm</th>
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<tr>
<td>organic substrate</td>
<td>acetate</td>
<td>UASB effluent</td>
</tr>
<tr>
<td>background respiration rate (gm⁻²d⁻¹)</td>
<td>3.5 ± 1.23 (14)</td>
<td>5.2 ± 0.50 (5)</td>
</tr>
<tr>
<td>maximum respiration rate (gm⁻²d⁻¹)</td>
<td>13.4 ± 1.21 (2)</td>
<td>10.1 ± 3.30 (12)</td>
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<tr>
<td></td>
<td>12.6 ± 1.27 (2)</td>
<td>11.3 ± 0.86 (5)</td>
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DISCUSSION AND CONCLUSIONS

The particular suitability of the biofilm monitoring system for biofilm respiration performance is demonstrated by the results of the acetate experiments (Fig. 3). The respiration of acetate caused a strongly increased respiration rate until the acetate concentration decreased to a limiting level. As a result of the observed background respiration, after circa 20 hours the total respiration has reached the equivalent of total acetate removed. This phenomenon indicates that the background respiration is the result of oxidation of some internal organic substrate absorbed by the biofilm in the period prior to the testing period. Consequently, the background respiration may be regarded as the maintenance level for the oxygen consumption. On the basis of net respiration (i.e. total respiration corrected for the background respiration level), about 58% of the acetate removed was calculated to be actually oxidized (Fig. 5). This figure is only valid under circumstances of sufficient availability of both acetate and dissolved oxygen.

The overall relations between the acetate removal rate and the corresponding respiration rate on one hand, and the concentrations of acetate and dissolved oxygen on the other hand (Fig. 5), seem to answer the 0-order kinetic model for substrate concentrations exceeding the corresponding minimum concentration. Although the scattering of the measurements does not allow a full verification of the $\frac{1}{4}$-order/0-order concept for biofilm kinetics (LaMotta 1976a, b; Harremoës, 1978), it seems reasonable to adopt $\frac{1}{4}$-order kinetics for substrate concentrations lower than the transition concentration. Moreover, the characteristic relation between the biochemical oxidation rate for internal substrate (background respiration) and the dissolved oxygen concentration (Fig. 6) strongly favours the $\frac{1}{4}$-order/0-order kinetic model.
Fig. 4. COD removal performance and simultaneous respiration of the UASB effluent biofilm sample submerged in the corresponding effluent
Effect of the bulk substrate concentration on acetate removal and simultaneous total respiration by the UASB effluent biofilm sample; dissolved substrates: acetate (Fig. 5a) and dissolved oxygen (Fig. 5b). Based on the discussed biofilm removal kinetics for acetate and the corresponding respiration, illustrated by Fig. 3, 5 and 6, it seems reasonable to adopt the 5-order/0-order kinetic model for both the removal and respiration of any dissolved organic substrate. The schematic course of the reaction rates for a hypothetical substrate are given in relation to the dissolved organic substrate concentration, in presence of sufficiently available oxygen (Fig. 7a), and also in relation to the concentration of dissolved oxygen in presence of sufficiently available organic substrate (Fig. 7b). Taking into account the background respiration for oxidation of internal substrate already present in the biofilm, the constructed graphs indicate that the difference between the total respiration and the background respiration may be regarded as the result of oxidation involved with the external substrate removed. Further, the difference between the maximum levels of substrate removal and the total respiration may be regarded as substrate removal involved biomass production. In the case of acetate a biomass yield of 0.45 gg⁻¹ is calculated (Fig. 5), for reactor conditions enabling maximum reaction rates.
Mechanisms and kinetics of COD removal

Within certain restrictions, the substrate concentration can be substituted by the biofilm loading rate. The relations shown in Fig. 7a indicate that biofilm growth, defined as positive biomass yield, can only occur for substrate concentrations (or loading rates) exceeding a certain maintenance level $C_0$ (or loading rate $L_0$). Maximum biofilm growth or substrate removal is obtained for substrate concentrations exceeding the transition concentration $C_{sub}$ (or loading rate $L^*$). On the other hand, in case these values are exceeded dramatically in continuously operated reactors, it is unavoidable that a substantial part of the substrate or waste is lost by discharge of the reactor effluent. Fig. 7b indicates that substrate oxidation occurs for oxygen concentrations exceeding the transition concentration for the background respiration ($C_{ox,b}$), whereas the maximum substrate oxidation is possible only if dissolved oxygen levels are maintained exceeding $C_{ox}$. Since the waste concentration restrictions set for discharge of effluents generally result in values lower than $C_{sub}$, the design of a RBC installation treating dissolved organic waste should be based on a concentration/loading rate couple for the final stage or compartment, causing $k$-order removal kinetics organic substrate limitation, viz. $C_{sub}$ and $L_{sub}$, and $C_{ox}<C_{ox}$.

In Fig. 4 it is shown that, in comparison to acetate, the oxidation of UASB effluent COD is of minor importance in the total removal mechanism. After 5 hours the respiration accounts for about 8%, 10% and 20% of the removal of COD$_t$, COD$_f$, and COD$_d$ respectively. In Fig. 4 it is also shown that during the first 5 hours of this particular experiment, COD$_c$ is removed very efficiently almost without being oxidized. These results indicate, firstly that removal processes other than biochemical oxidation are accounting for short-term COD removal, and secondly that the background respiration accounts for the bigger part of the total respiration, the net COD oxidation being of minor importance. Spanjers and Klapwijk (1987) also observed this phenomenon for organic matter elimination by non-nitrifying activated sludge, and they suggested a rapid physical process, probably adsorption, followed by biochemical oxidation at a low rate. The rapid removal of COD$_c$ is also reported by Särner (1981), who observed high COD$_c$ removal rates in the upper compartments of trickling filters.
Since no significant distinction is found for the COD removal characteristics for the measurements in the RBC units, compared to the biofilm monitoring system measurements-in the COD concentration ranges up to 200 gm⁻³ (CODₐ), 300 gm⁻³ (COD₈) and 400 gm⁻³ (COD₇)- (Fig. 2), it is demonstrated that short-term complete submergence of the biofilm is no obstacle for biofilm COD removal studies. Furthermore, the difference observed for the removal characteristics of COD₈ compared to COD₇ and COD₉ corresponds to the results of continuously loaded biofilm reactors, presented by Rusten (1984), and Bovendeur and Klapwijk (1986). Therefore, it may be concluded that biofilm performance studies, carried out in the biofilm monitoring system, are significant for attached biofilm performance in general. The extremely high COD₈ removal rates observed (Fig. 2), which are still directly proportional to the COD₈ concentration or COD₈ loading rate, point to biofilm adsorption processes rather than biochemical oxidation.

The estimation of the biomass yield involved with COD₇ degradation as demonstrated for acetate, is not allowed because of the COD adsorption processes. However, for demonstration purposes only, COD₇ is adopted as COD fraction approximating the removal characteristics of dissolved biodegradable substrate as illustrated in Fig. 7. This assumption is supported by the 0-order COD₇ removal rates observed (Fig. 2) and results presented earlier (Bovendeur and Klapwijk, 1986). Based on this assumption, and combining the removal kinetics for the COD₈ and COD₇ fractions (Fig. 2 and 7), Fig. 8 is constructed, schematically illustrating the proportional contributions by the removal of COD₈ and COD₇ in COD₉ removal, as functions of the corresponding COD concentrations or loading rates. It appears from Fig. 8 that the transition concentration for COD₇ (c₇O₇,f) is also significant for the kinetic order of the resultant COD₉ removal and, obviously, the reaction constant for COD₉ removal kinetics highly depends on the COD₈/COD₇ ratio. Based on the adoption of the ½-order/0-order kinetic model for biofilm removal of COD₇ and 1-order kinetics for the removal of COD₈, the possible kinetic orders of the resultant COD₉ removal are listed in Table 2.

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The overall result may explain why so many empirical formulas can be found in literature describing COD₉ removal by biofilm reactors. Further, the removal of COD₇—with a rather constant COD₇/COD₈ ratio as a result of pre-sedimentation-described by a hyperbolic function (Rusten, 1984) may also be explained by the possible combination of pseudo ½-order and 1-order kinetics for loading rates varying from relatively low values up to values exceeding the transition loading rate L₈COD₉,f in some degree. In addition, the results presented earlier by Bovendeur and Klapwijk (1986) are almost certainly explained by the presented combination of COD removal kinetics, based on c₇COD₇,f 100 ± 20 gm⁻³, 0-order COD₇ removal rate 30-40 gm⁻³d⁻¹, and a strongly varying COD₈/COD₇ ratio.

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Table 2. Kinetic Order of COD₉ removal for possible COD₇/COD₈ ratios in relation to the COD₈ concentration (COD₇,f).

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Mechanisms and kinetics of COD removal

As a consequence of the combined results, illustrated by Fig. 8, the final stage or compartment of a RBC reactor treating waste water composed of COD$_S$ and COD$_f$ mixtures, should be designed and operated for COD$_f$ concentrations not severely exceeding $c_{\text{COD}_f}^*$, whereas a certain COD$_S$ is admissible. However, since excess sludge production is the total of COD$_S$ adsorbed and the biomass yield resulting from COD biodegradation, high COD$_S$ loads will lead to dilution of the active biomass in the biofilm by high excess sludge production due to high COD$_S$ adsorption. Therefore, high COD$_S$ loads should be prevented. It should be noted that COD$_f$ in the presented schematic approach should be replaced by COD$_d$ or even better by BOD$_d$ (dissolved Biochemical Oxygen Demand).

The overall conclusion of the results is that a RBC reactor loaded with significant amounts of dissolved suspended organic matter may be described as a reactor in which the biofilm oxidizes only a part of the dissolved organic matter and acts as a catalyst in the coagulation and flocculation of fine suspended solids.
Fig. 8. Schematic presentation of fixed-biofilm (reactor) performance in a mixture of dissolved and suspended COD

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