Bio-kinetics of organic removal in EAAS reactor for co-treatment of refinery wastewater with municipal wastewater.

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Abstract: The refinery wastewater (RWW) is very complex in nature, which need energy intense treatment. Thus, it is difficult for developing countries to manage the treatment of RWW. The feasible option to tackle the problem is co-treatment with municipal wastewater (MWW). In the present study, co-treatment of RWW (0, 10, 20, 40, 60 and 80) % with MWW was investigated in a bench scale extended aeration activated sludge (EAAS) reactor. The result indicate that the maximum organic removal was achieved at 20% RWW, which was 91.84%. However, first order substrate removal model and Stover-Kincannon model achieve the coefficient of correlation value of 99.17% and 99.14% respectively, which clearly indicate that these models can be implemented to predict the performance of reactor. Furthermore, designing of the EAAS treatment plant can be conducted for co-treatment of RWW with MWW.

1. Introduction
The components of wastewater produced from the petroleum refinery are complex and recalcitrant. The removal of such recalcitrant pollutants is complex and involves high levels of energy. From one tonne of processed crude oil, approximately 3.5 to 5 m³ of wastewater is produced. For the handling of oily wastewater, biological methods such as the membrane bioreactor (MBR), upflow anaerobic sludge blanket and biological aerated filter reactor have been used [1-6]. Nevertheless, inherent disadvantages, such as high capital and operating/maintenance costs, technological sophistication, etc., are defined by such existing technologies. The technological feasibility and economic viability of the treatment processes, especially for developing countries, are reduced by these limitations [7]. Thus, the co-treatment of refinery wastewater (RWW) with municipal wastewater (MWW) can be one of the easiest solution to the entire problem [8].

The functional behaviour of the activated sludge relies on the presence of a microbial community composed of particulate and dissolved organic matter decaying bacteria, fungi, protozoa, and various other micro-organisms [9]. The main producers and decomposers that derive energy directly from dissolved organic matter are bacteria and fungi [10, 11].

In the wastewater treatment research articles, several models for biomass growth processes have emerged. As a substrate for analysis, universal parameters such as COD, BOD and NH₄⁺-N were used under the hypothesis that the removal was mainly attributable to aerobic biodegradation. First order substrate removal model, Stover and Kincannon (1982) model [12] and Monod (1949) model [13] are well established model implemented to study the kinetics for predicting reactor performance and design of reactor [14, 15].
In the present study, well known kinetic models were studied to predict the performance of extended aeration activated sludge (EAAS) reactor for organic removal, of the co-treatment of RWW (0, 10%, 20%, 40%, 60% and 80%) with MWW.

2. Methodology

2.1. Wastewater: Source and Composition
The refinery wastewater (RWW) in 0, 10%, 20%, 40%, 60%, and 80% was co-treated with municipal wastewater (MWW). The investigation was an attempt to determine the suitable percentage of RWW for co-treatment with municipal wastewater to reduce the load on refinery wastewater treatment plant.

2.1.1. Municipal wastewater (MWW)
The municipal wastewater was collected from Sewage Treatment Plant (STP) at Universiti Teknologi PETRONAS (UTP). The organic concentration of MWW was in the range of 300 – 350 mg COD/L, with pH of 7.1.

2.1.2. Refinery wastewater (RWW)
The refinery wastewater (RWW) was collected from one of the Malaysia’s oil refinery. The RWW was stored in a sealed container and kept in a cold room at 4°C to avoid microbial biodegradation activity and composition change. The concentration of organics and nutrients of RWW was 1200 mg COD/L and 9.3 mg NH₃–N/L, 3.7 mg TP/L respectively, with pH of 6.7.

2.2. Reactor set-up and start-up period
A lab scale extended aeration activated sludge (EAAS) reactor was used in the study to evaluate the performance for co-treatment of percentage of RWW with MWW. The EAAS reactor was fabricated with Plexiglas acrylic with working volume of 21 L. The dimension of aeration zone was 31 cm × 16 cm. The air was diffused through stone diffuser with concentration of 2.5 to 4.0 mg DO/L, which was monitored regularly with DO meter. The influent was continuously fed into the reactor with flowrate of 21 L/day, hence HRT was 1 day. The study was conducted at room temperature of 27°C. The schematic view of complete experimental set-up has been illustrated in Fig. 1. The inoculum of biomass was collected from STP, UTP. Considering, that the EAAS reactor is suitable for longer SRT, the selected SRT was 40 days by which volume of biomass was determined to be 1.1 L. The biomass was acclimatized in the reactor for 13 days before feeding with (0, 10, 20, 40, 60, and 80)% of RWW.

![Figure 1. Schematic diagram of experimental setup. (1) Influent tank. (2) Centrifugal pump. (3) AC supply. (4) Peristaltic pump. (5) Aeration zone. (6) Clarifier. (7) Effluent tank. (8) Air diffuser. (9) EAAS reactor.](image-url)
2.3. Bio-kinetic modelling
In fundamental science of biological processes, mathematical models are used to test the theories, assess the meaning of relationships between variables, direct the experimental design, and determine the outcomes of the experiment [16]. These models have also been used to monitor and forecast the efficiency of the operation of the treatment plant and to refine the configuration of the plant and the effects of pilot scale-up tests [17]. Simplified and established models, with fewer variables, are currently implemented to evaluate the biological reactor performance or design, which are easier to control and essential for industrial applications. The following well know bio-kinetic models were studied for the prediction and performance of the reactor [18, 19].

2.3.1. First order substrate removal model
In a CSTR system the rate of change of substrate concentration can be expressed as Eq. (1), assuming the occurrence of first-order kinetics.

\[- \frac{ds}{dt} = \frac{Q}{V_R} \times S_0 - \frac{Q}{V_R} \times S_e - k_1 S_e \]  

Furthermore, it can reduced to Eq. (2) under steady state condition the rate of change of substrate (dS/dt) is insignificant.

\[ \frac{S_0 - S_e}{HRT} = k_1 S_e \]  

where, \( S_0 \) = influent substrate concentration (mg COD/L), \( S_e \) = effluent substrate concentration (mg COD/L), \( HRT \) = hydraulic retention time (day), \( V_R \) = Volume of reactor (L), \( Q \) = flowrate (L/d), \( k_1 \) = first order substrate removal rate constant.

After plotting \((S_0 - S_e/HRT)\) versus \(S_e\) from Eq. (2), the value of \( k_1 \) can be obtained from the slope of the line.

2.3.2. Stover–Kincannon model
The Stover–Kincannon model is applied to study the substrate utilization rate, which is expressed as function of the organic loading rate. However, the effective volume of the reactor is used here [12, 20]. The model is expressed as;

\[ \frac{ds}{dt} = \frac{U_M \times (Q \times S_0 / V_R)}{K_b + (Q \times S_0 / V_R)} \]  

where \((dS/dt)\), the rate of substrate utilization is defined in Eq. (4)

\[ \frac{ds}{dt} = \frac{Q}{V_R} \times (S_0 - S_e) \]  

After linearization it can be expressed as Eq. (5)

\[ \frac{V_R}{Q \times (S_0 - S_e)} = \frac{K_b}{U_M} \frac{V_R}{Q \times S_0} + \frac{1}{U_M} \]  

After plotting \(HRT/(S_0 - S_e)\) versus \(HRT/S_0\) a straight line will be obtained, intercept and slope of the line are equal to \(1/U_M\) and \(K_b/U_M\), respectively.

where \(U_M\) = maximum substrate removal rate (mg COD/L.d), \(K_b\) = saturation value constant (mg COD/L.d).

2.3.3. Monod model
In 1942, Jacques Monod proposed a model to elucidate the growth of microorganism [13]. The equation based on the substrate mass balance equation for continuous-flow stirred tank reactor (CSFTR) is illustrated in Eq. (6). Thus, rate of substrate utilization based on Monod equation can be written as Eq. (7).

\[ \frac{ds}{dt} V_R = Q S_0 - Q S_e + V_R R_{SU} \]
\[ R_{SU} = -\frac{kX_M S_e}{X_M + S_e} = -\frac{S_0 - S_e}{HRT} \]  

(7)

After linerization of Eq. (7) we get Eq. (8).

\[ \frac{(HRT)X_M}{S_0 - S_e} = \frac{K_s}{k} \frac{1}{S_e} + \frac{1}{k} \]  

(8)

where, \( R_{SU} \) = substrate utilization rate (mg COD/L d), \( X_M \) = biomass concentration in the reactor (mg VSS/L), \( K_s \) = monod half-velocity constant and \( k \) = maximum specific substrate utilization rate.

After plotting \([X_M HRT/(S_0 - S_e)]\) versus \((1/S_e)\), the value of \( K_s \) and \( k \) can be determined from slope and intercept of the curve.

According to microorganism mass balance for CSFTR, Eq. (9) the Monod equation for specific growth rate is illustrated in Eq. (10). Under steady state condition Eq. (10) can be simplified as Eq. (11).

\[ \frac{dx}{dt} V_R = QX_i - QX_M + V_R R_G \]  

(9)

\[ R_G = \frac{\mu M X_M S_e}{K_s + S_e} - k_d X_M \]  

(10)

\[ \frac{1}{MCR_T} = \frac{\mu M S_e}{K_s + S_e} - k_d = -\frac{R_{SU}}{X_M} - k_d \]  

(11)

After plotting \(1/MCR_T\) versus \(-R_{SU}/X_M, k_d\), and \(Y\) values can be considered from intercept and slope of the graph, respectively.

The quantity of mean cell residence time were obtained using Eq. (12):

\[ MCR_T = \frac{v_R X_M}{(Q-Q_w)X_e - Q_w X_w} \]  

(12)

3. Results and discussion

The study executed on EAAS for co-treatment of RWW with MWW shows a significant effect with maximum COD removal efficiency of 91.84% at 20% of RWW. The overall summary of the study is illustrated in Table 1. To study the performance of the reactor few well established kinetic models were studied such as; first order substrate removal model, Stover–Kincannon model, and Monod model.

| RWW (%) | Operation period (days) | MLSS (mg/L) | MLVSS (mg/L) | OLR (kgCOD/m³.d) | Influent TCOD (mg/L) | Effluent TCOD (mg/L) | Removal Efficiency (%) |
|---------|-------------------------|-------------|--------------|------------------|---------------------|---------------------|------------------------|
| 0       | 1‒23                    | 5812        | 3030         | 0.026            | 486                 | 26                  | 91.44                  |
| 10      | 24‒42                   | 5052        | 2953         | 0.054            | 573                 | 54                  | 90.50                  |
| 20      | 43‒68                   | 4961        | 2955         | 0.068            | 828                 | 68                  | 91.84                  |
| 40      | 69‒93                   | 4775        | 2345         | 0.057            | 1207                | 102                 | 91.51                  |
| 60      | 94‒117                  | 3836        | 1712         | 0.177            | 1794                | 177                 | 90.13                  |
| 80      | 118‒140                 | 4017        | 2113         | 0.279            | 3015                | 291                 | 90.35                  |

3.1. First order substrate removal model

The slope of the straight line of plot between \((S_0 - S_e/HRT)\) and \(S_e\) as stated in Eq. 2, represent the value of \(k_1\), which is 9.0643 d⁻¹. The coefficient of correlation (\(R^2\)) is 0.9917, which clearly state that this model is suitable to predict the performance of EAAS reactor for the co-treatment of RWW with MWW. The following Fig. 2 is the graph of \((S_0 - S_e/HRT)\) versus \(S_e\).
3.2. Stover–Kincannon model

The plot of $\frac{HRT}{(S_0 - S_e)}$ versus $\frac{HRT}{S_0}$ as represented in Fig. 3, determine the value of $U_M$ and $K_b$ as stated in Eq. (5). The value of intercept ($1/U_M$) and slope ($K_b/U_M$) from the graph is 0.0028 (mg COD/L.d)$^{-1}$ and 0.3695 respectively. Hence, the value of $U_M$ and $K_b$ is 357.14 mg COD/L.d and 131.96 mg COD/L.d respectively. The value of $R^2$ is 0.9914, which represents that this model fits well for the experimental data. Stover–Kincannon model can also be used to predict the output of the reactor and also to design the reactor.

3.3. Monod model

Fig. 4 represents the plot between $[X_{ML} HRT/(S_0 - S_p)]$ versus $(1/S_p)$, from the equation of straight line we can determine the value of $K_S$ and $k$. The slope ($K_s/k$) and intercept $(1/k)$ of the curve from the plot is 152.32 and 5.9022 respectively. Hence, the value of $K_S$ and $k$ is 25.807 mg COD/L and 0.169 mg COD/mg VSS d, respectively. The coefficient of correlation ($R^2$) value, which is 0.7081, indicates that the experimental value does not fit with this model. Henceforth, this model cannot be implemented with good precision.

**Figure 2.** The plot for first order substrate removal model bio-kinetic.

**Figure 3.** Stover-Kincannon model plot.
4. Conclusions
The following points can be concluded from the present study of bio-kinetics of organic removal for the co-treatment of RWW with MWW in EAAS reactor.

- The investigation shows that with 20% of RWW mixed with MWW the organic removal efficiency is maximum, which is 91.84%.
- Among the bio-kinetics, which were studied, the first order substrate removal model and stover-kincannon model gave the high value of coefficient of correlation, which were 99.17% and 99.14%. Thus, these models can be implemented to design EAAS reactor for co-treatment of RWW with MWW.
- Finally, it can be stated that co-treatment of RWW with MWW can be feasible, which can reduced the load of refinery wastewater treatment plant.

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