Evaluation of Biological Kinetic Parameters Under Variable Solids Retention Times to Enhance the Efficiency of Pharmaceutical Wastewater Treatment

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Abstract

The protection of human health and the environment is a crucial measure of national development, especially with increasing dependence on pharmaceutical industries due to the rise of diseases. These industries, while essential, produce hazardous wastewater that poses serious environmental and public health risks. Effective treatment of such wastewater is therefore critical. This study focuses on optimizing the activated sludge process for pharmaceutical wastewater treatment through the determination of key biokinetic coefficients: maximum specific growth rate (μmax), half-velocity constant (K_s), yield coefficient (Y), decay coefficient (K_d), and substrate utilization rate (k). Laboratory-scale aerobic biological treatment was conducted in batch systems without solids recycling, across varying sludge retention times (SRTs). The results show that shorter SRTs (2–5 hours) enhance microbial activity, with higher values of k (3.2), μ_{max} (2.4) indicating faster substrate consumption and microbial growth. Conversely, Ks increases with SRT, reflecting reduced substrate affinity at shorter retention times. The decay coefficient (K_d) peaks at shorter SRTs (0.091), suggesting higher microbial turnover. Yield efficiency is highest at moderate SRTs (Y = 0.96 at 7.5–13.5 hours). Total volatile suspended solids (VSS) and biomass growth rates also peak at lower SRTs, indicating more active microbial processes. However, longer solids retention times (SRTs) favor overall substrate-to-biomass conversion efficiency. These findings underscore the importance of optimizing operational parameters such as SRT and HRT for designing cost-effective and sustainable pharmaceutical wastewater treatment systems.

Keywords: Biokinetic coefficients, Maximum specific growth rate, Half-velocity constant (K_s), Decay coefficient (K_d), Yield coefficient (Y), Wastewater treatment

1. Introduction:

Pharmaceuticals are vital for treating human and animal diseases, but rising global demand has led to increased production and significant pharmaceutical waste (Haider, 2023). This waste includes expired drugs, improperly stored medications, and unused pharmaceuticals, posing risks if not handled correctly. Improper disposal of pharmaceutical wastewater (PWW), rich in active ingredients and complex chemicals, threatens ecosystems, human health, and contributes to antibiotic resistance. The expansion of pharmaceutical use, especially during health crises like COVID-19, has intensified these concerns. Biological treatment methods are emerging as sustainable and effective solutions for managing PWW due to their ability to break down persistent organic pollutants (Dawood, *et al.*, 2023). Common pharmaceutical contaminants include antibiotics, hormones, analgesics, and cardiovascular drugs, many of which are now recognized as emerging environmental pollutants ((Ortúzar, *et al.*, 2022). Traditionally, biological wastewater treatment design was based on empirical parameters like hydraulic and organic loading rates, offering only a basic framework. Current, design approaches have advanced to include both empirical data and biological kinetic models that describe processes such as microbial growth and substrate utilization. These models use equations to calculate key parameters like reactor volume, biomass production, and effluent quality. Incorporating metrics like the food-to-microorganism ratio and mean cell residence time (MCRT) allows for more precise and efficient system design. This data-driven approach improves performance, adaptability, and compliance with regulatory standards. Biokinetic coefficients used in the design of activated sludge processes include specific growth rate(μ), maximum rate of substrate utilization per unit mass of microorganisms (k), half velocity constant (K_s), maximum cell yield (Y), and endogenous decay coefficient (K_d) (Sanghamitra, *et al.*, 2021). Biokinetic coefficients help match the right reactor type with the specific treatment goals and wastewater characteristics. They also inform decisions about bioaugmentation the process of adding specialized microbial cultures to enhance treatment. If kinetic data shows poor performance by native microbes, introducing a consortium with better *μmax* and higher tolerance can dramatically improve outcomes.

The prime objective of this study is to determine biokinetic coefficients K_s, k, Y, K_d, μmax for the design of activated sludge process, to treat pharmaceutical wastewater by conducting aerobic biological treatment studies in the laboratory using a bench scale reactor without solids recycle system.

2. Materials and Methods

2.1. Wastewater Characterization

The pharmaceutical industrial wastewater utilized in the present study was collected after physicochemical treatment processes. Standard analytical protocols were used for characterization of wastewater (APHA, 2005). Key parameters assessed included Chemical Oxygen Demand (COD), Biochemical Oxygen Demand over five days (BOD_5), pH, and the presence of various organic and inorganic contaminants such as residual active pharmaceutical ingredients (APIs), nitrates, phosphates, heavy metals, and total dissolved solids (TDS). The BOD: COD ratio of the wastewaters was in the range 4.3 - 6.9, which is higher and potential biological wastewater treatment required.

2.2. Description of system set up

In the present study, a laboratory-scale reactor with a working volume of 5 L was employed to determine the biological kinetic coefficients relevant to the treatment of pharmaceutical wastewater. The reactor was operated in batch mode over a period of 10 to 15 days, under controlled conditions, and subjected to varying solids retention times (SRTs) and hydraulic retention times (HRTs). This approach was designed to evaluate the influence of operational parameters on the removal efficiency of chemical oxygen demand (COD) and other organic pollutants. To monitor the treatment performance and assess microbial activity, daily measurements were conducted for influent COD (COD_{in}), effluent COD (COD_{out}), pH, and mixed liquor volatile suspended solids (MLVSS). These parameters provided the necessary data to calculate key kinetic coefficients. The experimental setup and monitoring strategy facilitated a comprehensive understanding of how different SRTs affect the biodegradation potential of the activated sludge system when treating high-strength pharmaceutical effluents.

2.3. Analytical methods

Both treated and untreated pharmaceutical wastewater samples were analyzed for key physicochemical and biological parameters using standard methods (APHA, 2005). The reactor performance was closely monitored on a daily basis, focusing on influent and effluent COD (COD_{in} & COD_{out}), pH, mixed liquor suspended solids (MLSS), and mixed liquor volatile suspended solids (MLVSS) to understand the efficiency of pollutant removal and microbial growth.

2.4. Startup of reactor

Initial the reactor was started with small volume of wastewater for acclimatization of microbes. After obtaining the desired quantity of biological solids (MLVSS) the reactor was operated in continuous mode with various HRTs. MLVSS concentration was also monitored daily during the startup phase to understand the aerobic biomass growth in the reactor. Effect of various SRTs on efficiency of pharmaceutical wastewater was carried out with withdrawal of specific quantity of sludge from the reactor. Each SRT was maintained for minimum 7 to 10 days. COD utilization over the period of time was analysed.

The reactor operation started with a small volume of pharmaceutical wastewater to allow for the acclimatization of microbial biomass to the specific characteristics of the influent. During this period, the reactor was operated in batch mode, and the concentration of mixed liquor volatile suspended solids (MLVSS) was monitored daily to track the growth and establishment of aerobic biomass. Once a sufficient concentration of biological solids (MLVSS) was achieved, the reactor was transitioned to continuous mode operation. Various hydraulic retention times (HRTs) were applied to assess their influence on treatment efficiency and microbial kinetics. To evaluate the impact of solids retention time (SRT) on the overall performance, specific volumes of sludge were systematically withdrawn from the reactor, thereby adjusting and maintaining different SRTs. Each SRT condition was sustained for a minimum of 7 to 10 days to ensure steady-state conditions.

Throughout the experiment, the utilization of chemical oxygen demand (COD) was analyzed over time to determine the reactor's organic removal efficiency under varying operational parameters.

2.5. Determination of Biokinetic coefficients

Bio kinetic coefficients were determined using data collected from pilot-scale experiments and relevant equations. The MLSS concentration was assumed to remain steady in each process. While the flow rate and solids retention time (SRT) were varied during the experiments, the tank volume was kept constant for all processes.

By plotting $\frac{(X\theta)}{(S0 - S1)}$ against $\frac{1}{S}$ we can derive K and Ks from the linearized form of the Monod equation. This method is widely used in environmental and biochemical engineering to determine microbial kinetics from batch or continuous reactor data.

$$\frac{\theta X}{S_0 - S} = \frac{K_s}{K}\frac{1}{S} + \frac{1}{K} = \frac{1}{U}$$

K_s: Half-velocity constant, mg sCOD L^{-1}

k: Maximum rate of substrate utilization, mgsCOD/mg VSS.d

X: Biomass concentration, mg VSS L^{-1}

Θ/Q: Hydraulic retention time, d

S: Effluent substrate concentration, mg sCOD L^{-1}

Following equation can be used to derive the yield coefficient (*Y*) and the endogenous decay coefficient (K_d) by rearranging and analyzing data from biological treatment processes.

$$\frac{1}{SRT} = Y U - K_d = Y \frac{S_0 - S}{\theta X} - K_d$$

SRT: Solids retention time, d

Y: Biomass yield, mg VSS/mgCOD

U: Substrate utilization rate, mgCOD/mg VSS.d

K_d: Endogenous decay coefficient, 1/d

S_o: In fluent substrate concentration, mg

By plotting , $\frac{1}{SRT}$ against$\frac{(S0-S1)}{\theta X}$, we can derive the yield (Y) and decay rate (K_d) can be determined from the slope and intercept, respectively.

3. Results and Discussion

3.1. Characterization of pharmaceutical wastewater

The wastewater exhibited a high organic load, with COD and BOD concentrations ranging from 5500–6500 mg $L^{-1}$and 800–1500 mg L^{-1}, respectively. Phosphate (PO_4^{3-}) and suspended solids (TSS) were found at concentrations well above allowable limits, indicating the presence of nutrient pollution and particulate matter. Total dissolved solids (TDS) and sulfate (SO_4^{2-}) were moderately high, with TDS nearly double the discharge standard. The pH values remained within an acceptable range (6–8.5).

Table 1 Characterization of pharmaceutical industry wastewater

Parameters	***Value***	**Effluent discharge standards**
pH	6 – 8.5	
COD (mg L^{-1})	5500 - 6500	250
BOD (mg L^{-1})	800 - 1500	30
NO_3-N (mg L^{-1})	15 to 35	10
NO_2-N (mg L^{-1})	20 - 52	35
NH4-N (mg L^{-1})	50 - 70	50
SO_4^{2-} (mg L^{-1})	80 - 200	300
PO_4^{3-} (mg L^{-1})	8 - 15	5
TSS	2000 - 2500	100
TDS	3500 to 4500	2100

3.2. COD removal efficiency at SRT (4 to 9 h)

The influent COD concentration (COD_{en}), measured prior to treatment, varied between 925 mg L^{-1} and 1050 mg L^{-1}. Across these experimental conditions, the batch reactor consistently demonstrated a high treatment performance, achieving COD removal efficiencies between 90% and 95%. These results indicate effective organic pollutant degradation within the studied HRT range.

Table 2 Parameter Assessment in Pharma Wastewater Treatment (SRT 4–9 hours)

S_o (COD_{in} – mg L^{-1})	S (COD_{out} – mg L^{-1})	SRT (days) (Q_c)	MLSS (mgL^{-1}) [X]
970	34	9.34	998
1070	45	7.34	1020
1050	57	5.78	890
925	69	4.5	996

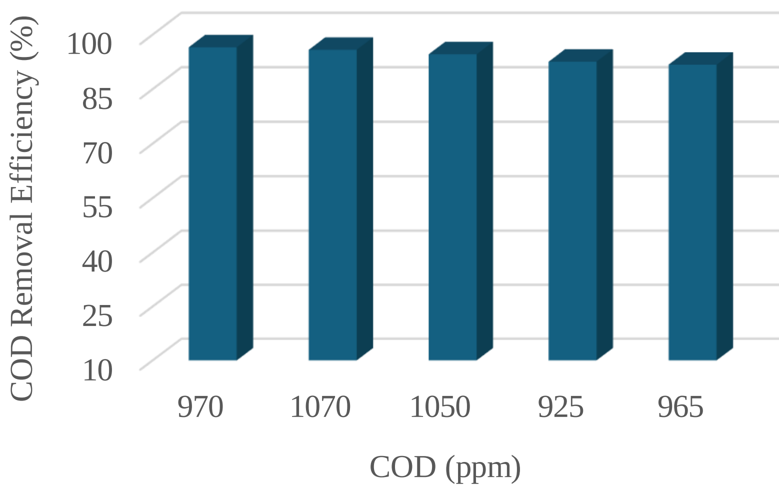


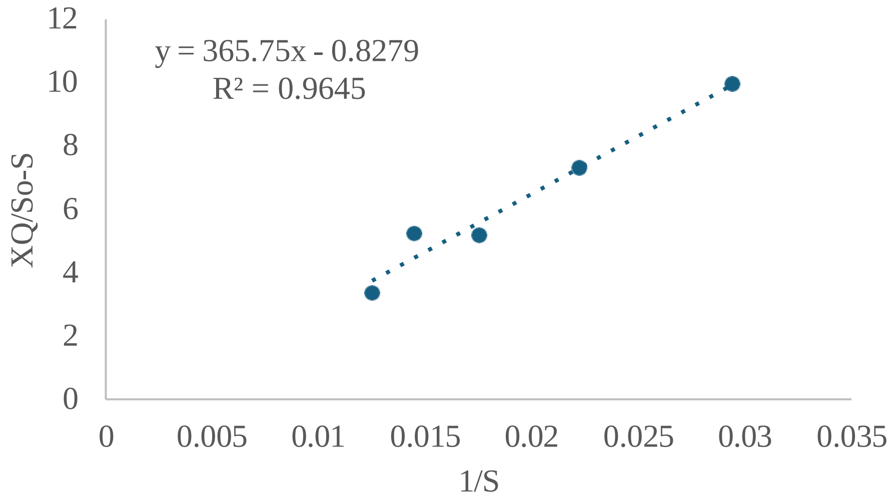
Figure 1 COD removal efficiency at SRTs (4 – 9 hours)

A comparative study was designed to survey the treatment efficiency of pharmaceutical wastewater containing Naproxen by Membrane bioreactor (MBR) and MBR with fixed-bed packing media (FBMBR). The results obtained from the present study indicated that COD removal efficiency for FBMBR (96.46%) was higher than that for MBR (95.33%) (Mokhtariazar, *et al.*, 2024).

3.3. Determination of *K, Ks, Y,* & K_d at varying SRTs (4–9 hours)

The maximum specific substrate utilization (k) at which microorganisms can consume substrate (e.g., BOD or COD) per unit of biomass. *Half-Saturation Constant (substrate concentration at half-max rate)* (K_s), reflects the affinity of microorganisms for the substrate (Alfeluo, *et al.*, 2021).

Based on the linear regression analysis of the experimental data, the maximum specific substrate utilization rate (*k*) was calculated to be approximately 1.207 day^{-1}, indicating the highest rate at which microorganisms can utilize the substrate under ideal conditions. The half-saturation constant (K_s) was determined to be approximately 441.76 mg L^{-1}, representing the substrate concentration at which the utilization rate reaches half of its maximum value. The coefficient of determination (R^2) was found to be 0.9645, signifying a strong linear correlation between the variables and indicating that the model provides a good fit to the observed data.



. **Figure 2 Determination of *k* and *Ks* at SRT (4 – 9 hours)**

Yield coefficient (Y), describes the amount of microbial biomass (MLVSS) produced per unit of substrate consumed. Endogenous decay coefficient (K_d) represents the rate at which biomass dies or is oxidized for maintenance in the absence of external substrate. Critical for understanding sludge age (SRT) and biomass stability. Endogenous decay rate (K_d) of 0.02 day^{-1} is considered low, meaning that the biomass is relatively stable and does not degrade rapidly, which is beneficial for maintaining steady microbial activity in the system. The yield coefficient (Y) indicates relatively high (0.83 mg VSS/g bsCOD), implying that a significant amount of microbial biomass is generated during substrate degradation. This could influence sludge production and handling needs.

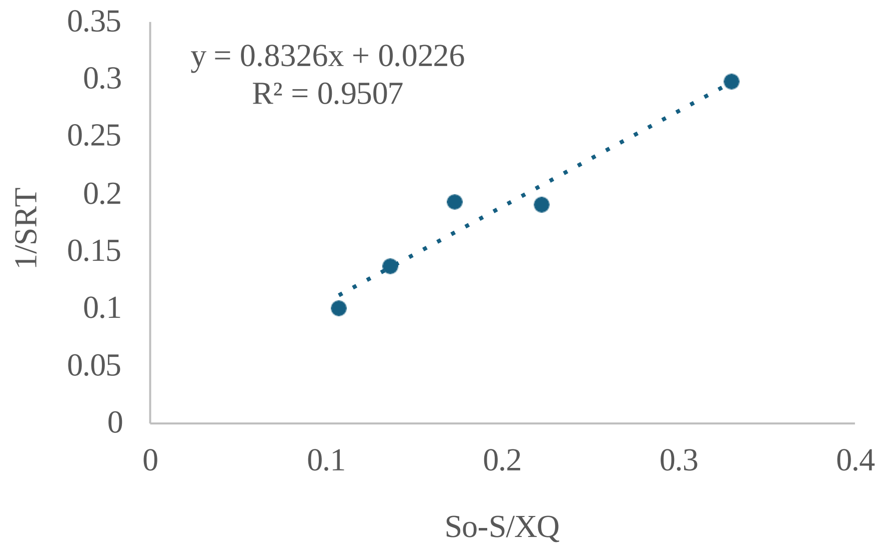


Figure 3 Determination of Y and K_d at SRT (4 – 9 hours)

3.4. COD removal efficiency at higher SRTs

The efficiency of COD removal was evaluated in a batch wastewater treatment system, with influent chemical oxygen demand (COD_{in}) levels ranging from 1250 to 1450 mg L^{-1}. For SRT in the range of 7 to 13 hours, over 94% COD removal efficiency in all cases, indicating excellent performance in degrading organic pollutants.

Table 3 Parameter Assessment in Pharma Wastewater Treatment (at higher SRT)

S_o(COD_{in} - mgL^{-1})	S(COD_{out} – mgL^{-1})	SRT (days) (Q_c)	MLSS (mgL^{-1}) [X]
1286	40	13.44	1286
1356	56	11.12	1356
1458	63	9.6	1458
1389	79	7.73	1389

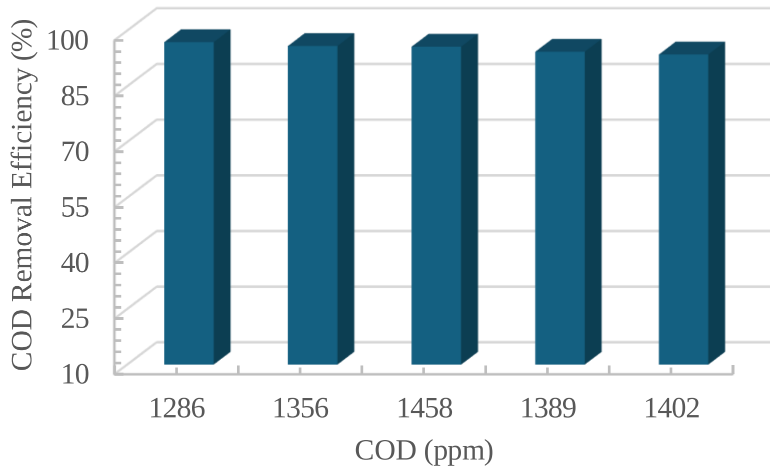


Figure 4 COD removal efficiency at higher SRTs

Although there was a slight decline in efficiency as influent COD increased, the variation remained marginal, suggesting the system's robustness even at higher organic loads. Surbhi, *et al.*, (2020) concluded that the peroxone process had 75–88.5% COD reduction efficiency at pH 5–11 in 3 h. Adsorption by activated char further reduced the COD to 85.4–92.7% for pH 5–11 in 2.5h from the effluent obtained from the pharmaceutical industry mainly contained anti-cancer drugs, anti-psychotic drugs, and some pain killers.

In a study conducted by Zhong *et al.*, (2003), a comprehensive analytical approach was employed to investigate the key parameters influencing the biodegradation of petrochemical wastewater. The researchers integrated Solids Retention Time (SRT) as a central evaluation metric to assess the performance and efficiency of the treatment process.

3.5. Determination of K, Ks, Y, & K_d at higher SRTs

For achieving biokinetic coefficients, the reactor was operated in batch mode at higher SRTs as shown in Table 4.8. System was operated at MLVSS in the range of 1200 to 1450 mg L^{-1} and CODin was in the range of 1250 to 1450 mg L^{-1}.

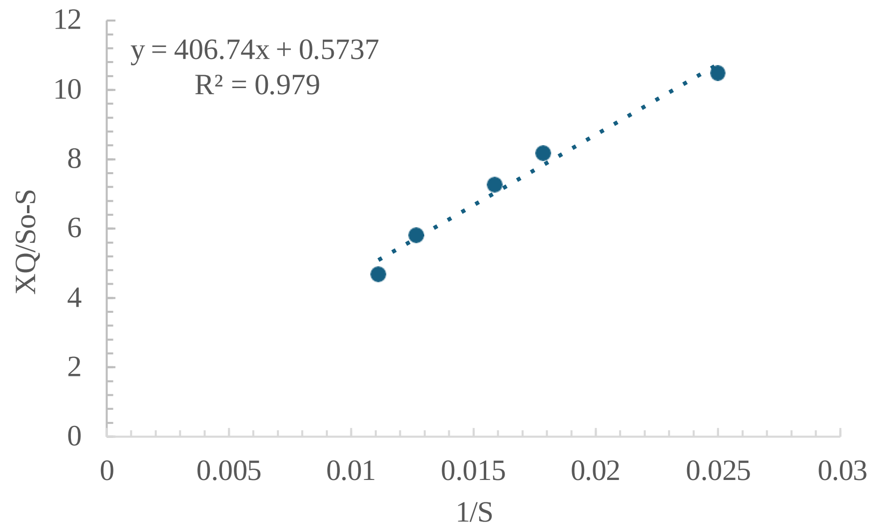


Figure 5 Determination of *k* and *Ks* at higher SRT

At higher SRTs for the treatment of pharmaceutical wastewater treatment evaluated the maximum specific substrate utilization rate (k) around 1.75 day^{-1}, indicating the maximum rate at which microorganisms can consume organic substrates when substrate concentration is not limiting. The half-saturation constant (K_s), which reflects the substrate concentration at which the utilization rate is half of the maximum, was found to be 713.58 mg L^{-1}.

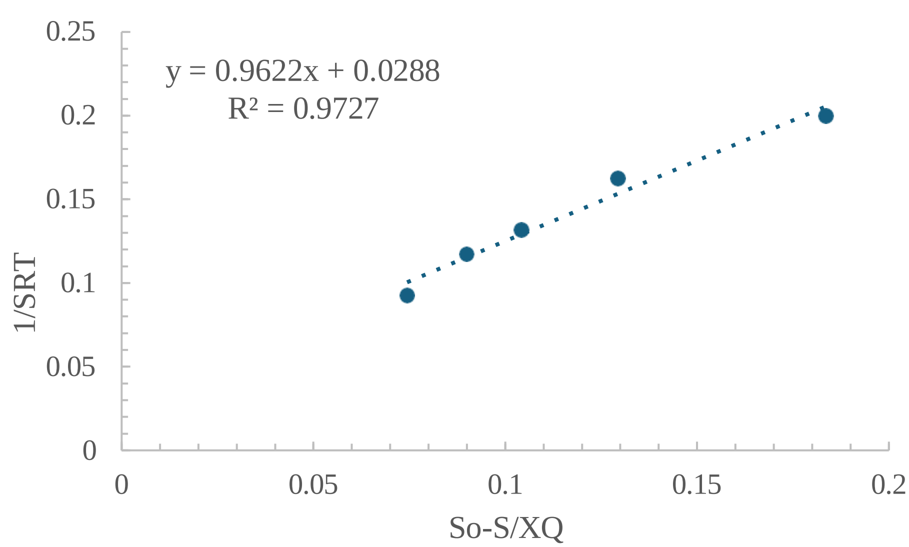


Figure 6 Determination of *Y* and K_d at higher SRT

The *endogenous decay coefficient* (K_d) was measured at *0.029 day*$^{-1}$, representing the rate at which biomass decreases due to cell death and maintenance processes. This low value implies that biomass decay is relatively minimal under the operational conditions. The *yield coefficient (Y)*, defined as the amount of biomass produced per unit of substrate consumed, was calculated to be *0.96 g VSS/g COD*, which suggests efficient biomass production from the available organic matter. Mardani *et al*., (2011) study, Y coefficient of extended aeration activated sludge process was determined 0.62-1.25 mg VSS/mg sCOD. They related this value to high SRT of extended aeration process. Naghizadeh *et al.*, (2014), conducted a study focused on evaluating the kinetic coefficients of a Membrane Bioreactor (MBR) system used for wastewater treatment. One of the key parameters assessed in their research was the biomass yield coefficient (*Y*), which reflects the amount of biomass (measured as volatile suspended solids, VSS) produced per unit of substrate consumed. Their findings indicated a yield coefficient of 0.67 g VSS/g COD, representing the efficiency of microbial growth in relation to organic matter degradation.

3.6. COD removal efficiency at lower SRTs

The experimental approach focused on systematically varying the input conditions (COD_{in}, SRT, and MLSS) to assess their impact on the performance of the reactor. The influent COD (S_0) values ranged from 1029 to 1130 mg/L, while the effluent COD (S) values were significantly reduced, ranging from 56 to 97 mg/L, indicating effective organic matter removal during treatment.

Table 4 Parameter Assessment in Pharma Wastewater Treatment (at lower SRT)

S_o (COD_{in} - mgL^{-1})	S (COD_{out} – mgL^{-1})	SRT (days) (Q_c)	MLSS (mgL^{-1}) [X]
1032	56	5.34	789
1029	70	4.02	880
1127	82	3.25	1036
1130	97	2.56	995

The COD removal efficiency across the four samples ranged from 91.46% to 94.57%, demonstrating the treatment system's high effectiveness in reducing organic pollutants. The highest removal was observed in the sample with an influent COD of 1032 mg/L and an effluent COD of 56 mg/L, achieving a 94.57% efficiency.

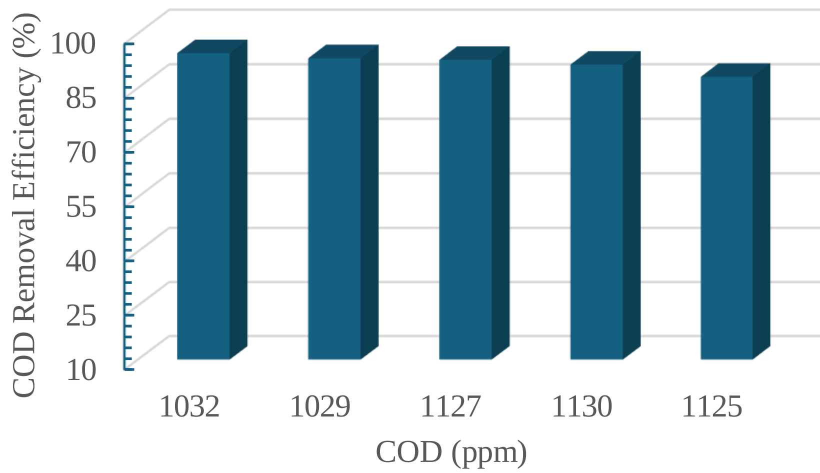


Figure 7 COD removal efficiency at lower SRTs

3.7. Determination of *K*, *Ks*, *Y*, & K_d at lower SRTs

The accuracy of the estimated values for *k* and K_s depends heavily on the quality of experimental data and the range of substrate concentrations tested. It's also important to note that these parameters are system-specific and can vary depending on factors such as microbial population, temperature, and substrate type (e.g., municipal vs. pharmaceutical wastewater). The given equation y=223.9x+0.3804 with a high R^2 value of 0.9744 indicates a strong linear correlation, suggesting that the linearized Monod model was effectively applied (Figure 8). In this context, the slope (223.9) represents K_s, and the intercept (0.3804) corresponds to 1/*k*, allowing accurate estimation of the kinetic constants *k* and K_s for the system.

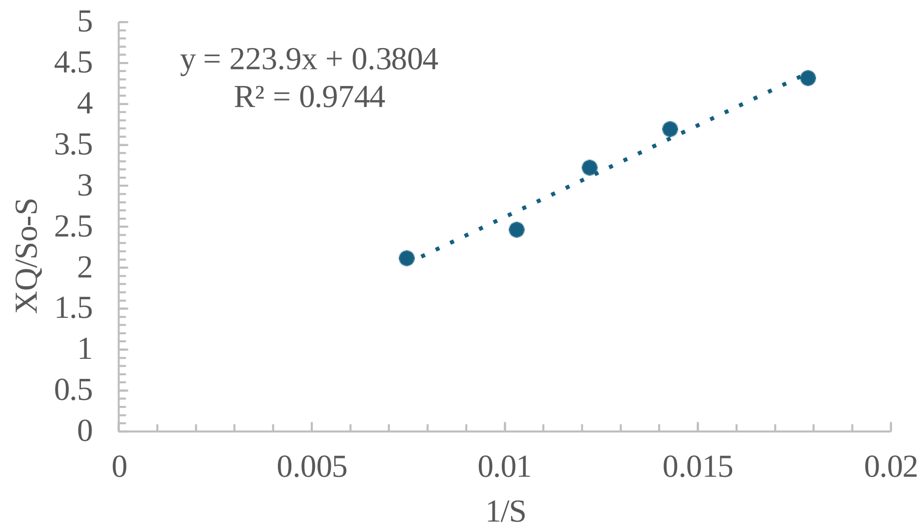


Figure 8 Determination of *k* and K_s at lower SRT

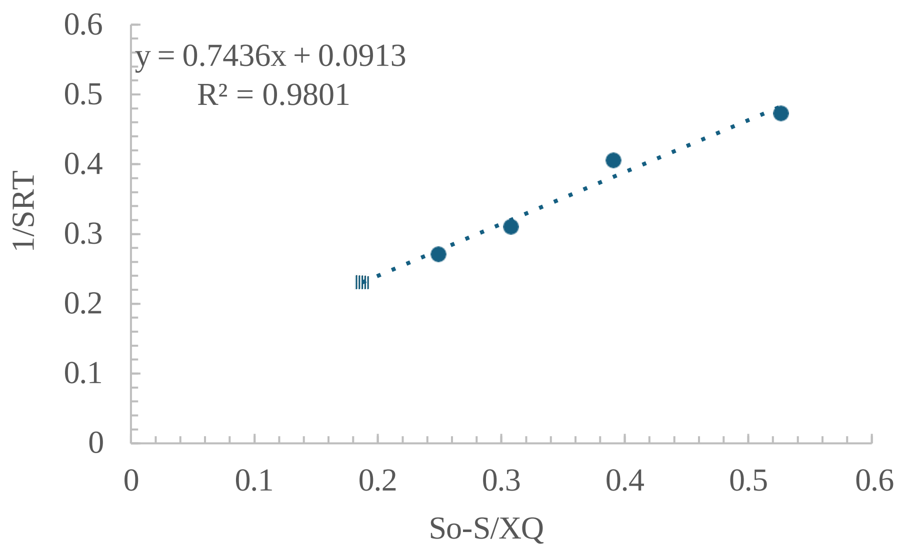


Figure 9 Determination of *Y* and K_d at lower SRTs

The *k* (Maximum Specific Growth Rate) of 3.2/day reflects a relatively high microbial growth rate under optimal conditions. The K_s (Half-Saturation Constant) of 736.51 mg/L implies that the microorganisms require a high substrate concentration to reach half of their maximum growth rate, indicating a low affinity for the substrate. The K_d (Endogenous Decay Coefficient) of 0.091/day suggests a moderate rate of biomass decay when no substrate is available. The *Y* (Yield Coefficient) of 0.75 mg VSS/mg BOD indicates that a significant amount of biomass is produced per unit of substrate consumed, highlighting an efficient conversion of substrate into biomass. The K_d (Endogenous Decay Coefficient) value of 0.091/day indicates a moderate rate of biomass decay in the absence of substrate. Y (Yield Coefficient) value of 0.75 mg VSS/mg BOD suggests that a significant amount of biomass is produced per unit of substrate consumed, indicating efficient conversion of substrate to biomass.

The kinetic coefficients obtained in this study provide valuable insights into the microbial growth and metabolic processes under the given conditions.

Conclusions

Kinetic coefficients k, K_s, Y, and K_d are essential for optimizing biological wastewater treatment. k indicates the pollutant consumption rate, K_s reflects microbial affinity for substrate, Y shows biomass yield, and K_d represents microbial decay. These parameters guide system design and efficiency. In this study, all four coefficients were evaluated in a batch system under different SRTs for pharmaceutical wastewater treatment.

The substrate utilization rate (k) increases as SRT decreases, peaking at SRT 2–5 hours (3.2), suggesting faster consumption by rapidly growing microbes. The half-saturation constant (K_s) rises with SRT, with the lowest value at SRT 2.5–5.6 hours (441.76 mg L^{-1}), indicating less efficient microbial uptake at shorter SRTs. The decay coefficient (K_d) increases significantly as SRT decreases, reaching a maximum of 0.091 at SRT 2–5 hours, due to higher microbial turnover.

The yield coefficient (Y) is highest at moderate SRTs (0.96 at SRT 7.5–13.5 hours), showing better biomass conversion efficiency. Maximum specific growth rate (μ_{max}) increases with decreasing SRT, highest at SRT 2–5 hours (2.4), favoring fast growers. In contrast, the actual specific growth rate (μ) shows no clear trend, being highest at SRT 2.5–5.6 hours (0.10), reflecting variability due to operational or microbial conditions.

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