

Effect of Wastewater Treatment on Bio-kinetics of Dissolved Oxygen in River Ravi

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Abstract

Waste management studies are usually done using calibrated and verified water quality models. Ravi River located in Lahore, Pakistan is receiving untreated wastewater from number of outfalls and surface drains and thus model calibration and verification are done using the data under the prevailing conditions. The water quality objectives can only be met with wastewater treatment wherein the model rate coefficients may change. The objective of this paper is to study the changes that may occur in these coefficients as a result of wastewater treatment. For this purpose, long-term BOD analyses have been carried out using river water and wastewater after different degrees of treatment. A laboratory scale biological reactor was used to study the effect of biological treatment on rate coefficients at 3, 6 and 10 days detention times. The study results show that CBOD biokinetic rate coefficient (K) reduces significantly from 0.25 day^{-1} for raw wastewater to 0.1 day^{-1} for the wastewater treatment for 3 days detention time in the biological reactor. Further reductions in the value of K to 0.07 day^{-1} and 0.05 day^{-1} occurred for a treatment level corresponding to 6 and 10 days detention times, respectively. The NBOD rate coefficient (K_n) was found to be 0.08 day^{-1} for 3 days detention time and 0.06 day^{-1} after treatment in the biological reactor at 6 and 10 days detention times.

Key Words: Dissolved Oxygen Management, Biokinetic rate coefficients, Nitrogenous biochemical oxygen demand, Nitrification, Carbonaceous Biochemical Oxygen Demand, Wastewater Treatment

1. Introduction

Waste management studies using calibrated and verified water quality models should be developed keeping in view the best use of the water body based on optimum level of wastewater treatment. Dissolved oxygen (DO) in rivers results from the combined effect of aeration and oxidation of organic matter. A commonly used one dimensional steady state mathematical model to predict DO level in the rivers receiving organic matter can be written as (Thomann & Mueller 1987);

$$D = D_o e^{-K_d t} + \frac{K_d L_o}{K_a - K_r} (e^{-K_r t} - e^{-K_d t}) + \frac{K_n L_{no}}{K_a - K_n} (e^{-K_d t} - e^{-K_n t}) \quad (1)$$

where D_o is the initial oxygen deficit, L_o is the ultimate Carbonaceous Biochemical Oxygen Demand (CBOD) in the river after mixing, L_{no} is the ultimate Nitrogenous Biochemical Oxygen Demand (NBOD) in the river after mixing, K_a is reaeration rate coefficient, K_r is the BOD removal rate coefficient and K_d is the river CBOD deoxygenation rate coefficient, K_n is the NBOD deoxygenation rate coefficient and "t" is the travel time in the river. K_a can be determined by using different empirical relationships. Singh and Ghosh (2007) used O'Connor's formula to determine K_a in DO modeling of river Yamuna, India. Jha and Ojha (2005) used Streeter Phelps Equation (i.e; Eq 1 without nitrification) to model DO in River Kali, India.

River water quality surveys are used to determine the rate coefficients to develop calibrated and verified models. These calibrated and verified DO models are used to determine the required degree of wastewater treatment to maintain DO standards to meet the specific use of the water body. The models can then be used to formulate river water quality management strategies. Mostly, the water quality models are developed, calibrated and verified under low flow conditions when the water body is receiving wastewater with a treatment level that could be different than the one required for desired river water quality.

The rate coefficients K_r , K_d and K_n are related to the oxygen sink and depend upon the nature of the wastewater and other physical, chemical and biological factors particular to the river. K_r is the removal rate of carbonaceous organic matter and is determined from river surveys and is equal to (Chapra 1997);

$$K_r = K_d + K_s \quad \text{-----} (2)$$

where K_s is the removal rate due to settling. K_d may be considered to consist of a component (K), characteristics of the type of wastewater and can be determined from the analysis of long-term BOD measurements. Significant portion of particulate BOD is removed up to the secondary level treatment (i.e; suspended solids < 30mg/L), therefore for such effluents K_s in equation (2) may be neglected

(Thomann & Mueller 1987). The other component “ ϕ ” is the characteristic of the conditions in the river and may include factors that are not included in long-term BOD analysis. These components can be related to each other as;

$$K_d = K + \phi \quad \text{----- (3)}$$

The wastewaters from urban areas are a mixture of carbohydrates, proteins and fats and vary in nature. With respect to biodegradation, their value changes with the level of treatment as readily biodegradable organic matter is first consumed (Thomann & Mueller 1987). As such the K_r , K_d and K_n which represent the biokinetic rates in the rivers will also change with the level of treatment. Bhargava (2008) developed a composite model considering the effect of settleable BOD for a river receiving wastewater from multiple outfalls by relating the rate constants with discrete and flocculent settling types.

Ha and Bae (2001) used built-in literature values of BOD decay coefficients in the software to assess the impact of different wastewater treatment levels for Bokha Stream, Korea. Radwan and Williams (2003) also used default values for different parameters in BOD and DO modeling of river Dender, Belgium. Maldenov & Strzepek (2005) used Streeter-Phelps equation for DO modeling of Notwane River, Botswana and used a depth based empirical relationship to determine K_d without any field measurements. Murty & Shallamudi (2006) used values of 0.25day^{-1} and 0.5day^{-1} for BOD deoxygenation rate and BOD decay rate respectively for modeling BOD and DO and reduced the deoxygenation rate to 0.2day^{-1} for 35% to 98% variation in wastewater treatment levels. No discussion was made of BOD decay rate while determining optimum level of treatment. Singh & Ghosh (2007) used a constant value of 1.3 day^{-1} of BOD deoxygenation rate coefficient to determine optimum BOD removal efficiencies for five wastewater drains discharging in river Yamuna, India. The main emphasis of these studies is on the improvement in computational techniques and use of software. The accuracy, with which a mathematical model can predict the field conditions, however depends upon the use of appropriate rate coefficients based on the type of wastewater being discharged into the river.

Ravi River is one of the most polluted rivers in Pakistan and is receiving large quantity of untreated municipal and industrial wastewater discharges from the city of Lahore through 5 wastewater outfalls and 2 surface drains (Fig 1) (WASA-LDA, 2001; WWF, 2007). The river under low flow conditions with about $10\text{m}^3/\text{s}$ discharge has turned almost into a wastewater drain (IPD – Punjab, 2004). The present conditions of the river require urgent implementation of appropriate control measures. For this purpose appropriate rate coefficients to use in the river DO

model are essential. The objective of this paper is to assess the effect of wastewater treatment on biokinetic rate coefficients to provide a more rational approach for water quality management of the River Ravi.

2. Methodology

Wastewater samples were collected from the Main Outfall pumping station, which is one of the major points of wastewater discharges from the city of Lahore into Ravi River. Biokinetic rate coefficients for CBOD and NBOD are determined by conducting log-term BOD analysis using river sample, raw wastewater, settled and filtered wastewater samples and biologically treated effluents from a bench scale biological reactor operated at different detention times.

3. Experimental Setup

The raw wastewater was first settled in a settling tank with a volume of 30.6 Liters (20cm x 51cm x 30cm). The settled wastewater was then shifted to the influent bottle of 20 Liters capacity to feed into the biological reactor. The schematic flow diagram and a picture of the bench scale biological reactor without solids recycle established at the unit process laboratory of the Institute of Environmental Engineering and Research (IEER), University of Engineering and Technology Lahore are shown in Fig 2a&b. The biological reactor was 31.4cm in length, 29.8cm wide and 27.2cm deep (i.e., 25.45 liters capacity). The wastewater from the feeding bottle was introduced to the aeration tank through a peristaltic pump to run the reactor at different detention periods. The peristaltic pump could be operated up to a flow of 2.0 L/day to have up to 12 days detention time in the aeration tank.

The reactor was run for about two month to develop adequate biomass to achieve biological treatment. Mixed-liquor Suspended Solids (MLSS) was used as a measure of the biomass. The biological treatment including nitrification is dependent on certain factors such as, sufficient number of nitrifiers, phosphates, an alkaline environment (i.e., $\text{pH} \cong 8$) and about 1-2 mg/L of oxygen in the water (Thomann & Mueller 1987). The pH was maintained above 7.5 throughout the laboratory experimentation period.

Oxygen was provided to the aeration tank with the help of six equally spaced diffuser stones with the size of (25mm x 25mm x 25mm) each. Oxygen levels of more than 3mg/L were maintained and observed throughout the experimentation period. When MLSS were reached to a concentration of more than 200mg/L, the reactor was operated at varying detention times of 3, 6 and 10 days to achieve different degrees of biological treatment. At every detention time three samples were taken on different days to determine degree of treatment before analyzing data for rate calculation. The effluent from the aeration tank was settled for 1 hour in a 3L beaker prior to long-term BOD analysis.

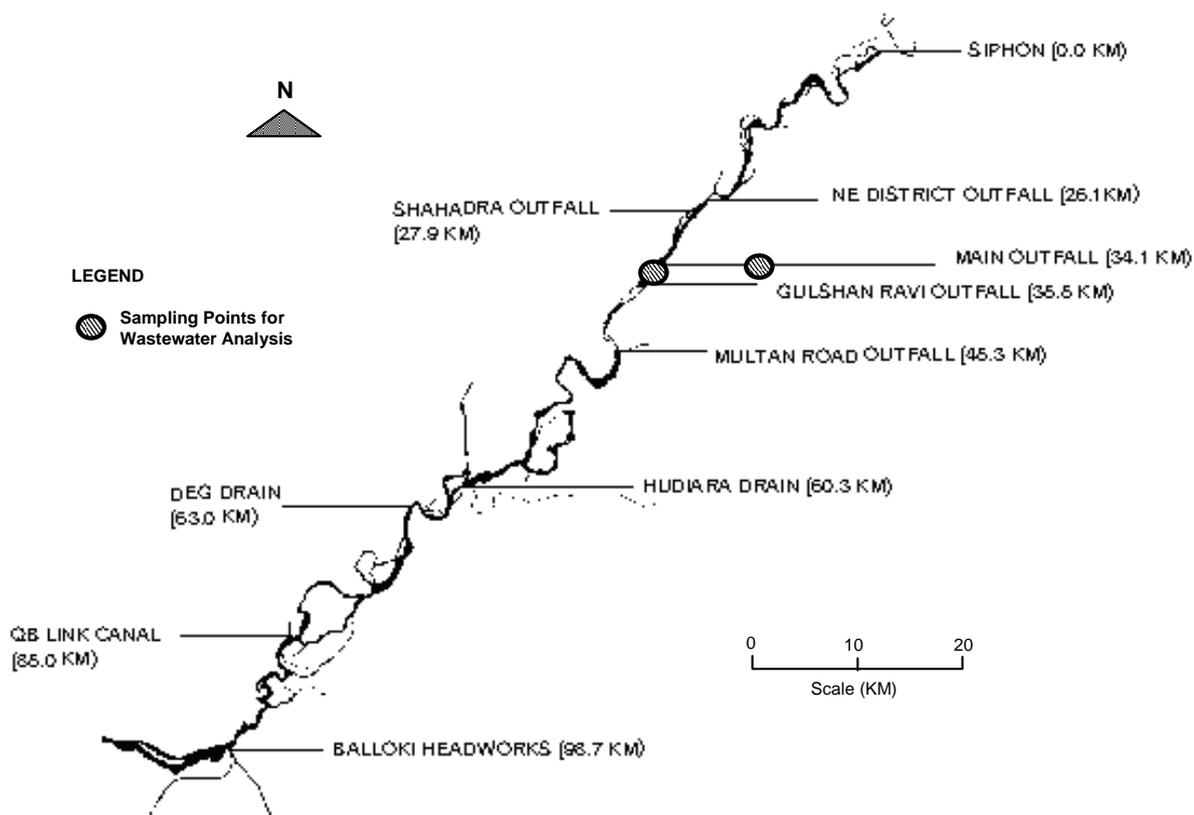


Fig 1: Location of wastewater outfalls and surface drains along the Ravi River

4. Materials and Methods

Long-term BOD tests were conducted for both BOD and CBOD by preparing two different sample sets using standard 300mL bottles as per Standard Methods for the Examination of Water and Wastewater (APHA 1998). Nitrification was inhibited in one set by adding 10mg/L Nitrification Inhibitor, Formula 2533, Hach Co., Loveland (i.e., 2-chloro-6-trichloro methyl pyridine) in the dilution water to determine CBOD. Dissolved oxygen in all the bottles and aeration tank was measured with Standard Winkler method (APHA 1998). With each sample a set of blank and a set of GGA (glucose – glutamic acid) check as per standard quality control procedures were also performed and found within in the limits prescribed in the Standards Methods. CBOD rate constant “K” and NBOD rate constant “K_n” were determined using Thomas Method (TM) (Thomas 1950).

Temperature and pH of all the samples collected from the main outfall were measured with the help of HACH, Portable meter. MLSS and Mixed-liquor Volatile Suspended Solids (MLVSS) were measured according to Standard Methods for the Examination of Water and Wastewater (APHA 1998). Total Kjeldahl Nitrogen (TKN) and Ammonia Nitrogen (NH₃-N) of all the samples analysed for long-term BOD analysis were also measured as per Standard Methods (APHA 1971 & 1998).

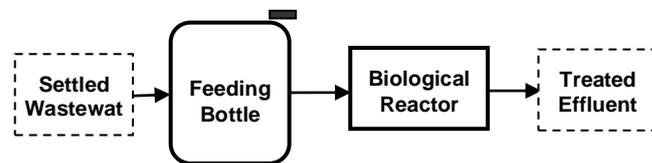


Fig 2a: Schematic flow diagram of laboratory wastewater treatment process



Fig 2b: Laboratory setup of biological reactor used in this study

5. Results and Discussion

5.1 Long-Term BOD Analysis

The results of the long-term BOD measurements are given in Table 1 and Fig 3 & 4. Raw and settled samples show similar behavior, except the difference in ultimate CBOD (CBODU). In both the cases the exersion of NBOD starts at about 5 days. In the river sample collected under low flow conditions the exersion of NBOD started on 3rd day due to presence of sufficient nitrifiers in river water. In case of filtered sample, however, it started after 7 days due to lesser population of nitrifiers which may have been removed during filtration.

The long term BOD results for biologically treated effluent at detention times of 3 days, 6 days and 10 days are shown in Fig 4. It can be seen that effluent treated with 3 days detention time has a higher oxidation behavior in first 5 to 7 days than the other two cases. Nitrogenous demand as higher component of NBOD (i.e., difference between BOD and CBOD curves) also shows that effluent contains more than 3mg/L of NH₃-N and about 20mg/L of NBOD. Even the effluent treated with 6 days detention time contains about 2mg/L NH₃-N. However, effluent receiving treatment for 10 days has only 0.4mg/L of NH₃-N which shows that nitrification has almost been completed and very little overall organic matter (i.e., about 10 mg/L CBODU) is left as well (Table 2).

The BOD results were analysed using Thomas Method to determine ultimate BOD (BODU), CBODU, ultimate NBOD (NBODU) and biokinetic rate coefficients, K and K_n for CBOD and NBOD respectively. The ultimate values and biokinetic rates along with measured ammonia nitrogen (NH₃-N), Total Kjeldahl Nitrogen (TKN) and the ratios between CBODU/CBOD5 are presented in Table 2. Coefficients of correlation (R²) for Thomas Method were found to be between 0.89 and 0.99 for CBOD.

Canale & Owens (1995) used Thomas method to determine K from long-term BOD analysis by inhibiting nitrifies. They estimated K value of 0.11 day⁻¹ from long-term analysis of secondary treated effluent. Ultimate CBOD and NBOD values are shown in Fig 5. As a total of 4.57g of oxygen per gram of ammonia nitrogen is required to oxidize it completely (i.e; to convert into nitrates). Total Kjeldahl Nitrogen (TKN) in wastewater is present in the form of ammonia nitrogen (N_a) and organic nitrogen (N_o) which is also hydrolyzed into ammonia nitrogen (Thomann & Meuller 1987). Therefore ultimate NBODU (L_{no}) in Fig 6 is estimated as;

$$L_{no} = 4.57(N_o + N_a) \quad \text{----- (4)}$$

Significant decrease in BOD₅ of 160 mg/L for raw wastewater to a value less than 10mg/L for biologically treated wastewater is observed with increase in level of treatment. It can be seen in Fig 5 that after 3days of detention period in biological treatment, CBODU and NBODU are 30 mg/L and 22mg/L respectively, which show

presence of significant portion of nitrogenous organic matter in effluent.

Removal of both NH₃-N and TKN was observed in the same pattern with varying level of treatment (Fig 6). Organic nitrogen component can be estimated from the difference between TKN and NH₃-N in Fig 6. Both NH₃-N and TKN rapidly decrease with the start of biological treatment with a sudden drop of TKN value from 36mg/L in settled wastewater sample to 4.9 mg/L in biologically treated effluent at 3 days detention time. Effluents treated at 6 and 10 days detention periods contain only 3.3 mg/L and 0.8 mg/L TKN respectively, which shows more complete nitrification and lower NBODU values.

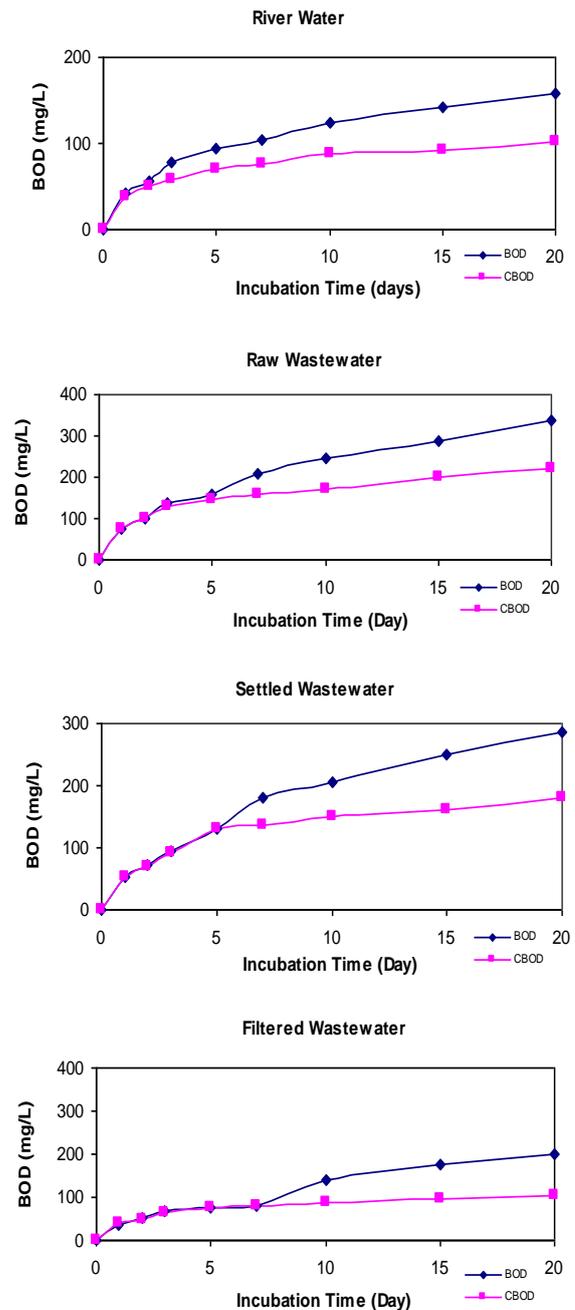


Fig 3: Long-term BOD results of raw, settled and filtered wastewater samples

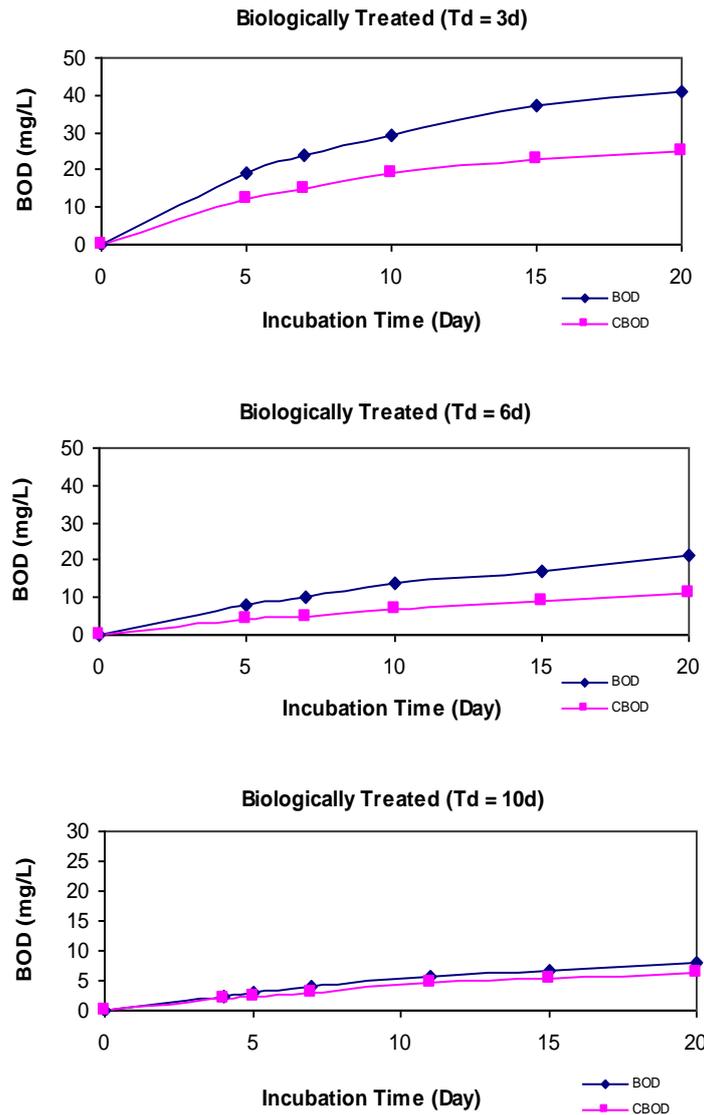


Fig 4: Long-term BOD results of biologically treated effluent at 3, 6 and 10 days detention time

Table 1: Summary of laboratory experimental data

Level of Treatment	BOD5 (mg/L)	BOD20 (mg/L)	CBOD5 _m (mg/L)	CBOD20 (mg/L)	CBOD20 / CBOD5 _m	TKN (mg/L)	NH ₃ (mg/L)
River Sample	95	159	59	102	1.44	13.9	9.1
Raw Wastewater	160	337	145	220	1.52	41	26.8
Settled Wastewater	131	285	130	180	1.38	36	21.2
Filtered Wastewater	78	200	75	105	1.4	31	18.2
Biologically treated effluent with 3days detention time	19	41	12	25	2.08	4.9	3.2
Biologically treated effluent with 6 days detention time	8.2	21.5	5	11	2.44	3.3	1.9
Biologically treated effluent with 10days detention time	2.9	7.9	2.3	6.4	2.78	0.8	0.4

*measured BOD

Table 2: Summary of analysis of laboratory data

Level of Treatment	CBOD				NBOD			
	CBOD _{5c} *	CBOD _U	K	R ²	CBOD _U /CBOD _{5c}	NBOD _U **	K _n	R ²
	(mg/L)	(mg/L)	day ⁻¹	TM*		(mg/L)	day ⁻¹	TM*
River Sample	82	112	0.26	0.94	1.37	57	0.22	0.82
Raw Wastewater	167	234	0.25	0.94	1.4	120	0.21	0.93
Settled Wastewater	132	193	0.23	0.96	1.47	110	0.2	0.87
Filtered Wastewater	86	116	0.27	0.95	1.35	105	0.21	0.98
Secondary treated effluent with 3days detention time	11.9	30	0.1	0.99	2.47	20	0.08	0.93
Secondary treated effluent with 6 days detention time	4.1	15	0.07	0.89	3.59	14.9	0.06	0.89
Secondary treated effluent with 10days detention time	2.3	10	0.05	0.94	4.19	2.1	0.06	0.64

* calculated BOD

** NBODU estimated using TM

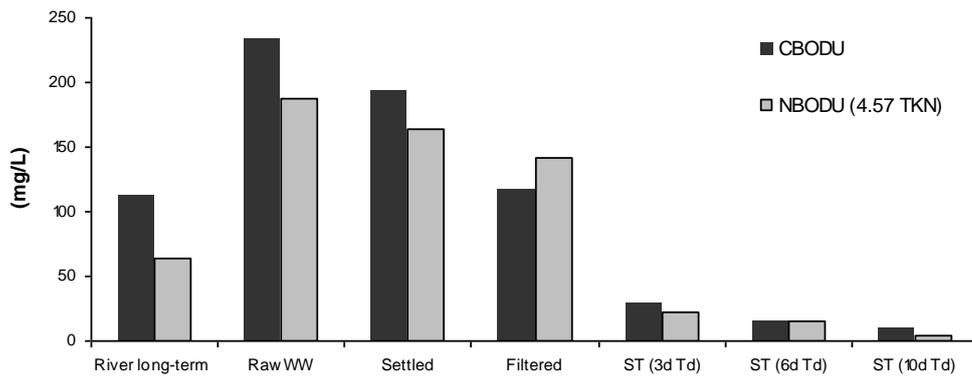


Fig 5: Effect of wastewater treatment on ultimate CBOD and NBOD

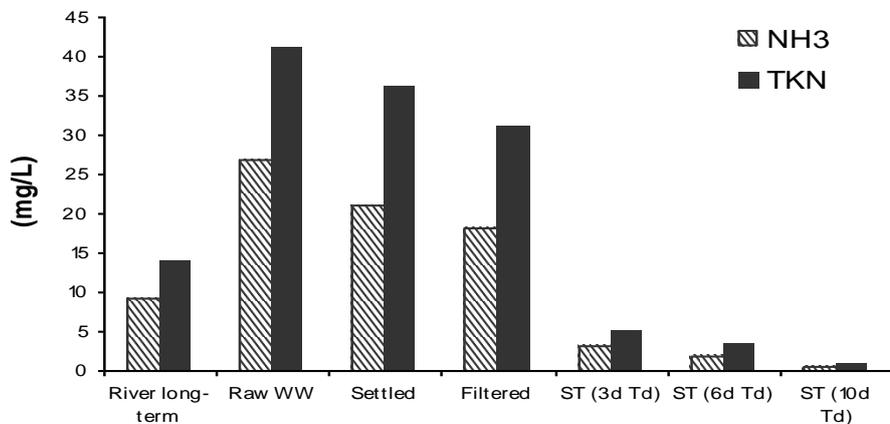


Fig 6: Measured values of NH₃-N and TKN for different treatment levels

NBODU values determined and were found to be lower than 4.57 TKN (Eq 4), which could be due to the presence of extremely slow biodegradable nitrogenous matter (Fig 7). However, in the case of 6 and 10 days detention periods in biological treatment the values are similar, which is due to increase in nitrification process. Biological treatment with longer detention times can provide more time to nitrifiers to oxidize even the forms of nitrogenous organic matter, which are difficult to biodegrade. In river sample the difference is also not significant due to presence of sufficient population of nitrifiers even at the start of the long-term BOD analysis (Fig 3).

Biokinetic Rate Coefficients of Wastewater

The biokinetic rate coefficients are calculated using the long-term BOD data shown in Fig 8. K value of 0.25 day⁻¹ for the raw wastewater is very close to K value of 0.26 day⁻¹ for the river sample. K and K_n values of 0.27 day⁻¹ and 0.21 day⁻¹ are highest in case of filtered sample (Fig 8) due to availability of readily biodegradable colloidal and dissolved portion of organic matter as compared to raw and settled wastewater. K for biologically treated effluent with 3 days of detention time has a higher value of 0.1 day⁻¹ than the K value of 0.07 day⁻¹ and 0.05 day⁻¹ for the effluents treated at 6 and 10 days detention times respectively. These results indicate that the biokinetic rate coefficient (K) decreases by a factor of 2.5 to 5 with increase in level of treatment showing that effluents treated from a biological treatment unit are less susceptible to biochemical oxidation, therefore have a lower BOD exertion rate. Chapra (1997) reported approximate range and average CBOD bottle rate coefficients of raw, primary treated and secondary treated wastewaters which are shown in Table 3. These results show decrease in K value by a factor of about 2.7 for wastewater treated from primary to secondary level.

Thomann & Mueller (1987) has reported that K_n is approximately equal to CBOD rate coefficient, i.e; 0.1 – 0.5 day⁻¹ at 20°C for deep large water bodies and can go up to 1.0 day⁻¹ for smaller streams. However, in this study K_n is observed to be lower than K for all types of wastewaters except biologically treated effluent at 10 days detention time. K_n varied between 0.08 day⁻¹ for biologically treated effluent with 3 days and 0.06 day⁻¹ for 6 and 10 days detention periods.

The change in the rate of biodegradation can also be represented by CBODU/CBOD5 ratio. These results are given in Fig 9. The CBODU/ CBOD5 ratios are calculated by the following equation;

$$\frac{CBODU}{CBOD5} = \frac{1}{1 - e^{-5K}} \quad \text{----- (5)}$$

where K is the CBOD bottle rate.

There is a marked increase in CBODU/ CBOD5 ratios with increase in level of biological treatment. The CBODU/

CBOD5 ratios of raw wastewaters is about 1.4, which is slightly higher than the literature values of 1.2 for raw wastewater in Table 3 (Chapra 1997). However, the CBODU/ CBOD5 ratio for settled sample is 1.47, which is slightly lower than the literature value of 1.6 for primary treated wastewater. This is due to the specific characteristics of Lahore wastewaters. These results also emphasize on the need of site specific measurements and analysis rather than relying on literature values for water quality management.

Table 3: CBOD bottle rate coefficients “K” and CBODU/ CBOD5 of municipal wastewaters

Degree of Treatment	K (day ⁻¹) @ 20°C		CBODU/ CBOD5
	Approximate range	Average	
Untreated/raw wastewater	0.2 – 0.5	0.35	1.2
Primary	0.1 – 0.3	0.2	1.6
Activated Sludge	0.05 – 0.1	0.075	3.2

(Chapra, 1997)

The CBODU/ CBOD5 ratios for biologically treated effluents based on degree of treatment in terms of detention time have a large range from 2.5 to 4.2. Biologically treated effluent with 3 days detention time has a CBODU/ CBOD5 ratio of 2.5 which is lower than the reported literature value of 3.2 in Table 3 for activated sludge process (Chapra 1997). However, the ratio increases significantly to 3.6 and 4.2 with increase in detention time from 3 to 6 days respectively (Fig 9). Such high ratios also reveal clearly that biodegradation decreases with increase in degree of treatment.

Bio-kinetic Rate Coefficients in Rivers

Canale and Ownes (1995) estimated K_d in the river receiving secondary treated effluent as 0.1 day⁻¹, which is very close to previously determined bottle rate “K” of 0.11 day⁻¹. Lung (1998) studied the effects of primary and secondary treatment without nitrification and with nitrification on the DO levels in Upper Mississippi River. Significant improvements were observed in the DO levels at higher levels of treatment. The river CBOD deoxygenation rate (K_d) was reduced from 0.27 day⁻¹ for primary treated effluent to 0.19 day⁻¹ for effluent that received secondary treatment. The K_d further reduced to 0.057 day⁻¹ for secondary treated effluent with nitrification, the value was also found very close to the bottle rate “K” of 0.05 day⁻¹ (Fig 10). These results show that K_d in the river was reduced by a factor of 1.4 to 5 when the level of wastewater treatment increases from primary to secondary and to secondary with nitrification.

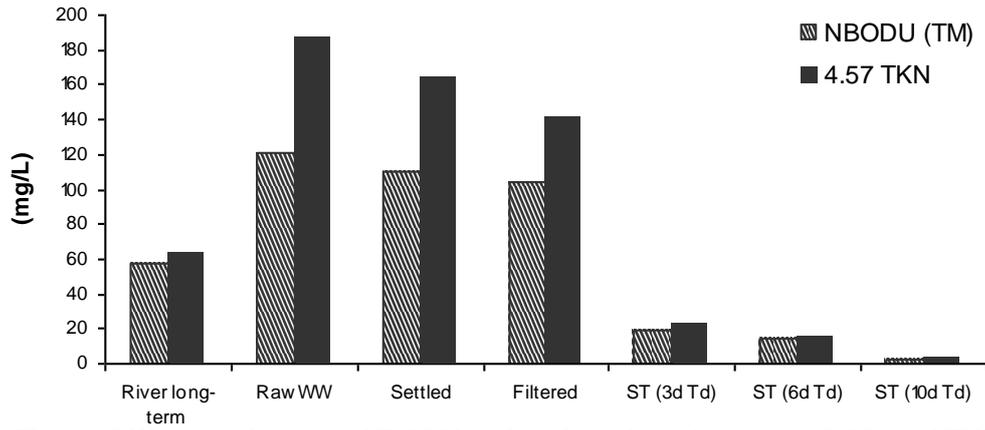


Fig 7: Difference between NBODU estimations from long-term BOD and TKN

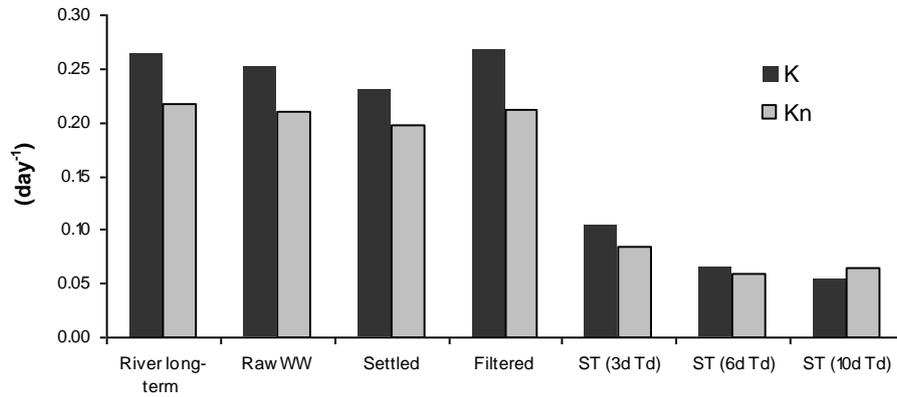


Fig 8: Variation in biokinetic rate coefficients with increase in level of treatment

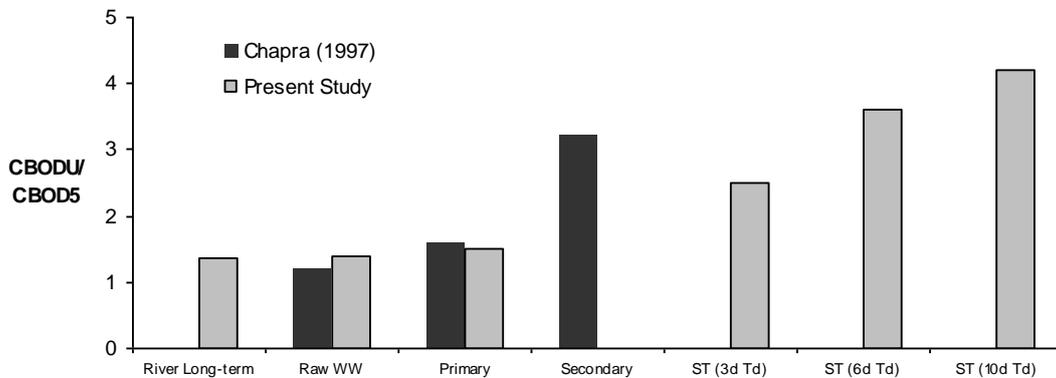


Fig 9: Comparison of different studies for effect of wastewater treatment on CBODU/ CBOD5

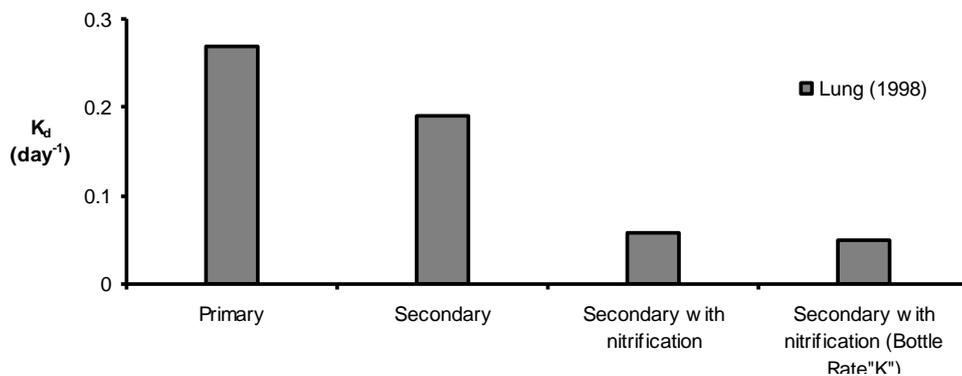


Fig 10: Comparison of different studies for effect of wastewater treatment on K (day⁻¹)

The change in K_d results from the changes in K and “ ϕ ” values (Eq 3). For a given river, it is reasonable to assume that “ ϕ ” will not change significantly with level of treatment. Thus the reductions in K_d values in the river as reported by Canale (1995) and Lung (1998) are mainly due to the decrease in the biodegradability of the wastewater with level of treatment as reflected by the rate coefficient.

As discussed earlier, K value of Lahore wastewater decreases significantly with increase in level of treatment. As such the K_d values in the River Ravi are also expected to decrease when treated wastewater will be discharged. Thus the K_d values in the DO model of River Ravi determined under present conditions will require adjustment when the model is to be used for the river receiving treated wastewater. Depending upon the level of treatment, the K_d values may be reduced a factor ranging from about 1.5 to 5.0.

Conclusions

The CBOD rate (K) first increases from 0.25 day^{-1} for raw wastewater to 0.27 day^{-1} for filtered sample due to presence of readily biodegradable organic matter. A direct relationship of K with different levels of biological treatment has been noted wherein K value reduces from 0.27 day^{-1} to 0.05 day^{-1} with increase in biological treatment levels. NBOD rate (K_n) of 0.21 day^{-1} was observed for both raw and filtered wastewater samples. However, in biological treatment, K_n value varies slightly between 0.08 day^{-1} to 0.06 day^{-1} for 3 and 10 days detention times respectively. Moreover, the residual carbonaceous organic matter after achieving nitrification also becomes more resistant to biodegradation, which results in higher CBOD_U/CBOD₅ ratios up to 4.2.

Biokinetic rate coefficients vary with levels of treatment from primary settling to biologically treated wastewater. The CBOD rate coefficient (K) in this study decreases about 5 times from settled sample to higher degrees of biological treatment. Whereas, a decrease of about 3 times was observed in NBOD rate coefficient (K_n) from settled sample to biologically treated effluent with 10 days detention time.

The deoxygenation rates in rivers decrease when wastewaters with higher level of treatment are discharged into them. This decrease in rate coefficients is mainly due to the change in biodegradability of wastewater as reflected by K and K_n . Moreover, the rivers receiving effluents treated at secondary level or higher the bottle rates are almost equal to the river rates.

As the Ravi River is currently receiving wastewater without any treatment, therefore the river rate (K_d) applicable to calibrated and verified DO model under present conditions is not appropriate for use in the development of strategies for water quality management of the Ravi River, wherein high level of treatment will be required. The results of the study suggest that the River Ravi

rate coefficient (K_d) will require reduction by a factor ranging between 1.5 to 5 depending on the level of treatment to achieve desired water quality objectives.

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