Chemical Oxygen Demand (COD) Fractions Characterization of Karachi Metropolitan Wastewater

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Summary: To prove the hypothesis that the inert products are given to environment due to biological degradation of substrate in activated sludge operations. This study was design to investigate the inert fractions of chemical oxygen demand (COD) in metropolitan effluent. An aerobic batch reactor system was experimentally setup and maintained up to 480 hours. At the end of operations, COD compositions of metropolitan wastewater were found to be S_{TO} = 131 mg/L, X_{SO} = 63 mg/L, C_{SO} = 178 mg/L, S_{SO} = 115 mg/L, S_I = 16 mg/L, X_I = 218 mg/L, respectively. At the end of operations, COD compositions of metropolitan wastewater were found to be S_{TO} = 131 mg/L, X_{SO} = 63 mg/L, C_{SO} = 178 mg/L, S_{SO} = 115 mg/L, S_I = 16 mg/L, X_I = 218 mg/L respectively.

This study is focused on inert COD fractions of metropolitan wastewater which consist of domestic as well as local industrial effluent. Soluble inert COD (S_I) must be determined for discharge standards since it did not give any reaction in activated sludge system and was given with wastewater discharge. However particulate inert COD (X_I) accumulated in system depending on sludge retention time due to it is only wasted from system by wasted sludge. Experimental techniques were used attained Zohu X. *et al.* [1, 2] in order to determine directly influent particulate and soluble inert fractions. The experimental study was carried out until COD profile reached to steady state or depletion of degradable substrate.

The conventional parameters of municipal characterization were as follows: total COD (C_{TO}) = 412 mg/L, total soluble COD (S_{TO}) = 131 mg/L, biochemical oxygen demand (BOD_5) = 197 mg/L, total biochemical oxygen demand (BOD_t) = 351 mg/L, total suspended solids (TSS) = 264 mg/L, ammonia nitrogen (NH_3-N) = 26.6 mg/L, grease & oil (G & O) = 17.5 mg/L and pH were 7.4 SU, respectively.

Introduction

Characterization of wastewater and activated sludge has been used for control and optimization of existing processes, and development of new processes. COD is a basis for organic matter measurements has replaced by biochemical oxygen demand (BOD) as the primary parameter in wastewater. The important aspect of organic matter characterization is the fractionation due to its rate of degradation [1, 2]. COD is used as a direct parameter to yield the stoichiometric equivalent of carbonaceous substrate [3], with the provision that its biodegradable fraction is ascertained [2, 4]. This fraction reflects the appropriate electron balance between substrate, biomass and the electron acceptor [3, 5]. COD fraction involves identification of inert and biodegradable COD together with readily biodegradable and slowly biodegradable fractions [4, 6]. The inert fraction may be further subdivided into soluble inert COD (S_I) and particulate inert COD (X_I) [7-10].

S_I in the influent bypasses the system without affecting the biochemical reactions in the reactor, whereas, the X_I is entrapped, accumulates in the activated sludge and leaves the system through the sludge wastage stream [3, 11, 12]. The experimental assessment of inert soluble and particulate COD of different wastewaters under aerobic and anaerobic conditions has also been studied [2, 13, 14].

The modeling and design of biological treatment (activated sludge) systems are essential aspect of environmental engineering [1, 14-16]. Conventional activated sludge models composed of single substrate and biomass components are useless in preceding days. Multicomponent models are chosen for both characterization of raw wastewater and explanation and understanding of activated sludge process [17-22]. Up to now, activated sludge models used assumed that effluent substrate

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concentration was independent of influent substrate concentration and substrate characterization of effluent and influent remained unchanged [1, 17-19]. A lot of research indicated that most of the residual substrate was produced by biomass and effluent substrate concentration related with influent of it. Both influent and effluent substrate components and components of biomass can be determined by using multicomponent activated sludge models recently [20, 23-29].

The important point on multicomponent models of activated sludge systems is determination of wastewater characterization. This depends on organic matter and characterization of wastewater [30-32]. COD parameter used for substrate determination can not give degradation of organic matter biologically [31]. Therefore, biologically degradable parts and inert fraction of COD must be determined since all modeling and calculations of design depend upon biodegradable COD. The determination of particulate and inert fractions of wastewater is also important in order to compliance the discharge standards and operating conditions [8, 32].

Inert COD components remain inert in both modeling & design of activated sludge and wastewater treatment system. It must also determine the soluble (S_P) and particulate microbial (X_P) products associated with biological growth and decay processes [2, 33]. Inert soluble COD (S_I) and inert particulate COD (X_I) leave the treatment system unchanged; however, X_I is entrapped in the sludge line [13]. Both S_I and X_I inert COD components in wastewaters and also soluble and particulate inert metabolic products produced in system must be determined in order to assess suitable operating conditions for correct modeling as well as design of the facilities [12, 34]. In this study, soluble and particulate inert COD fractions in wastewater of metropolitan effluent and residual soluble inert metabolic (X_P) products that comes from biological processes were experimentally investigated. Three aerobic batch reactors were used in order to determine inert COD fractions in wastewater composed of domestic and local industrial wastewater. Inert COD parameters were observed from batch reactors acclimated with wastewater, glucose and filtrated wastewater throughout 480 hours.

Results and Discussions

Various respirometric procedures have been proposed previously for estimating readily and slowly biodegradable COD fractions. Total soluble COD (S_{TO}) includes non-biodegradable (S_I) organics in influent wastewater and effluent, some part of biologically degradable COD (S_S+S_P) from residual biological oxidation and soluble COD produced as metabolic product COD (S_P). As a result, treated effluent generally includes more soluble inert COD than influent wastewater, since effluent soluble inert COD include various soluble inert products except soluble inert COD of inlet wastewater unchanged in reactor that is residual COD (S_R) [2, 10]. Influent particulate and soluble inert fractions were determined experimentally [2, 4] using three batch reactors, two with the wastewater to be studied and the third with glucose. One reactor with the total COD (C_{TO}), and the second with the total soluble COD (S_{TO}) and whereas the initial COD in the glucose reactor was adjusted to equal to S_{TO}.

The approach of this study was to determination of inert fractions of soluble COD. Three batch aerobic reactors were fed with Raw, Filtrated and Glucose (samples) shown in Table 1. The experimental reactors allow to run until all the biodegradable COD was depleted, and the COD profiles reached to stability and stay unchanged. As shown in Fig. 1, glucose soluble COD (S_{PG}) reach to stability condition, as soluble glucose contained no inert fractions. Total of S_I and S_{P1} reaches S_{R1} values beginning with S_{TO} value. Therefore, S_I value can be calculated as follows; where two reactors are operated with same S_{SO}. It is assumed that

$$(S_P)_{wastewater} \approx (S_P)_{glucose},$$

Y_I coefficient can be written by using S_I and S_{TO} and

Table-1: Experiment Performed on Raw, Filtrated Wastewater and Glucose Inert COD Results.

Reactors	Start of the Experiment	End of the Experiment	Duration (Hours)
Reactor I feed with Raw wastewater Soluble COD (mg/L)	131 (S_{TO})	34 (S_{R2})	480
Reactor II feed with filtered wastewater Soluble COD (mg/L)	127	27 (S_{R1})	480
Reactor III feed with Glucose Soluble COD (mg/L)	127	11 (S_{RG})	480

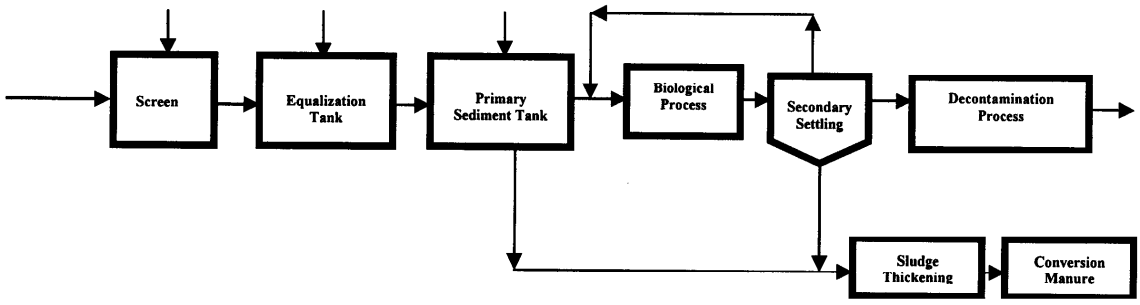

Fig. 1: Schematic of Metropolitan Wastewater Treatment Plant.

Y_{SP} stoichiometric coefficient can be formulated following equation given in Table-2.

Table-2: Evaluation of the COD experiments for the study.

Experimental Evaluation (Equations)	#
$S_I = S_{R1} - S_{PG}$, 27-110 = 16 mg/L	(1)
$Y_I = S_I/S_{SO}$, 16/115 = 0.139 mg/L	(2)
$Y_{SP} = (S_{R1} - S_I)/(S_{TO} - S_I) = S_{P1}/S_{SO}$ (27-16)/(131-16) = 0.113 mg/L	(3)
$S_{P2} = S_{R2} - S_I$, 34-16 = 18 mg/L	(4)
$C_{SO} = (S_{P2}/S_{P1})S_{SO}$ (18/11)115 = 188 mg/L	(5)
$X_I = C_{TO} - C_{SO} - S_I$, 412-188-16 = 208 mg/L	(6)

[2, 8]

The results of wastewater characterization are given in Table-3. Effluent samples were taken from equalization tank of metropolitan wastewater treatment plants shown in Fig. 2. COD fractions of metropolitan are given in Table 4, on average C_{TO} was 412 mg/L with a soluble fraction of 131 mg/L.

Table-3: Characteristics of Wastewater Used in Experimental Study.

Analytes/ Parameter	Concentration (mg/L)
Oxygen Demand Chemical total (C_{TO})	412±82.0
Oxygen Demand Chemical soluble (S_{TO})	131±41.8
Oxygen Demand Biochemical (BOD_5)	197±19.07
Oxygen Demand Biochemical total (BODt)	351±38.32
BOD_5/COD	0.478±0.06
Suspended Solids total (SSt)	264±39.57
Grease & Oil (G&O)	17.5±8.48
Nitrogen Ammonia (NH_3-N)	26.6±7.14
pH Value*	7.4±0.86

*SU

Experimental

In this study, metropolitan effluent (mixture of domestic comes from houses, hospital, and other utilities toxic and harmful wastewaters) were exploited. Generally metropolitan wastewaters have different properties than industrial effluents, depend upon various factors. Average wastewater flow rate during the seasonal variations were determined to be 31877 gallon per day (gpd) in summer and 22530 gpd in winter 2008. wastewater samples were taken from effluent of equalization tank in SITE treatment plant-1 (TP1) shown in Fig. 2.

Table-4: COD Fraction of Metropolitan Wastewater.

Analytes/ Parameter	Metropolitan wastewater sample (mg/L)
Total COD (C_{TO})	412
Total Soluble COD (S_{TO})	131
Total particulate inert fraction (X_{TO})	281
Inert COD	234
Soluble inert fraction (S_I)	16
Particulate inert fraction (X_I)	208
Total biodegradable COD (C_{SO})	188
Readily biodegradable soluble fraction (S_{SO})	115
Slowly biodegradable fraction (X_{SO})	63

Materials and Methods

The respirometric assessment of inert and readily biodegradable COD was performed using three batch reactors. Reactor I, II and III were fed with unfiltrated wastewater, filtrated wastewater and glucose with COD strength same as filtered wastewater respectively. All reactors were initially seeded with same amount of biomass concentrations (30-40 VSS mg/L) previously acclimated to a 50% wastewater + 50% glucose mixture. The reactors were constantly aerated to maintain a dissolved oxygen concentration of 6 to 8 mg/L. The biomass was acclimation was performed in fill and draw reactor operated in an aerobic condition at a sludge age of 5-7 days. Aliquots were removed from reactors every 30 to 60 min for oxygen utilization rate (OUR) measurements [35]. Soluble (filtrated) COD data were collected until the COD profiles

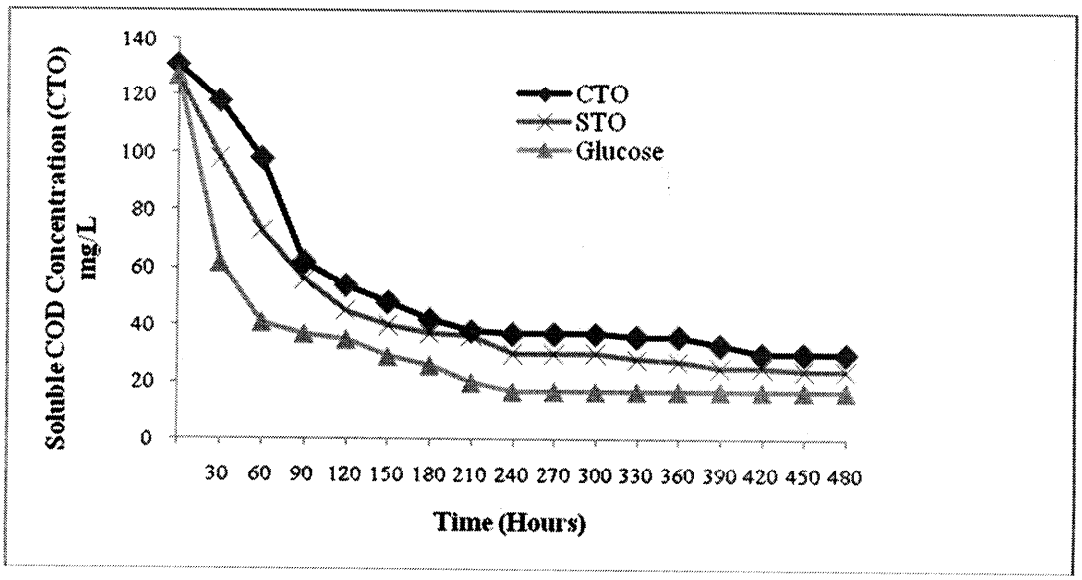

Fig. 2: Determination of X_I for the Metropolitan Wastewater.

reached stability. Any water loss from the reactors by evaporation was replaced by adding distilled water (15-20 mL) before measuring COD. Experiments were conducted at maintained room temperature 28 °C and a maintained pH of 7.0-8.0 by addition of buffers. Analysis was performed as defined in Standard Methods [36]. The soluble COD was defined as the filtrate through Millipore AP40 filters, also used in the determination of volatile soluble solids (VSS) and total suspended solids (TSS). OUR measurements were conducted with a SensIon95 OXI electrode DO meter. The activated sludge was supplied from Karachi Water & Sewerage Board treatment plant (TP-1) and used after (OUR measurement and nutrient flux adjustment) adaptation.

Conclusion

In order to determine soluble and particulate inert fractions of wastewaters and soluble inert metabolic products produced in system, batch experimental study was carried out. The results of this study are important for modeling, design and operation of activated sludge systems and compliance of discharge limits. The inert COD fraction was determined using the procedures proposed by Zohu *et. al.,* [2, 12]. Both soluble (S_P) and particulate inert microbial (X_P) products can be expressed as constant fraction of the influent biodegradable COD in that procedure.

Experimental study was conducted using three parallel batch reactors operated with raw wastewater, filtrated wastewater and glucose supplemented wastewater samples for ≈ 480 hours given in Table-1. In each reactor, total and soluble COD were monitored for a period long enough to ensure the depletion of all biodegradable substrate and mineralization of all biomass, so that the measured total COD (C_{TO}) and total soluble COD (S_{TO}) values reach their constant threshold level containing only initial inert COD and residual products. Experimental data were first evaluated according to equation 1 [2, 8] given in Table-2, yielding S_I =16 mg/L, SP_1 = 11 mg/L with corresponding coefficients of Y_I = 0.139 mg/L and Y_{SP} = 0.113 mg/L. Subsequently, S_{P2}, C_{SO} and X_I were found to be 18 mg/L, 188 mg/L, and 208 mg/L, respectively, by using equations 3, 4, and 5 shown in Table-2. With the experimental assessment of X_I and S_I the following initial composition of wastewater sample was determined shown in Table 4 that is C_{TO} = 412 mg/L, X_I = 208 mg/L, S_I =16 mg/L, C_{SO}= 188 mg/L.

The comparison of this composition with similar typical values shows a very good agreement for S_I, with the 25-40 mg/L range described in the literature corresponding to $S_I + SP_2$ = 34 mg/L in the present study given in Table-2. The X_I concentration of 208 mg/L is relatively high compared with the range in the literature 25-100 mg/L [22], 68 %

particulate COD in influent is inert. This is attributed to the fact that except domestic wastewater both hospital and laboratory wastewaters are given into wastewater biological treatment unit.

Evaluation of experimental study given in Table-5 indicated that 31.7 % and 68.2 % of total COD were soluble and particulate compounds. 32.03 %, 3.9 % and 52.9 % of total COD were soluble easy degradable organic material, soluble inert and particulate inert material, respectively.

Table-5: Evaluation of Experimental Results.

Parameters	Metropolitan Wastewater
S_{TO}/C_{TO}	31.7
X_{TO}/CTO	68.2
S_I/C_{TO}	3.9
X_I/C_{TO}	52.9
S_{SO}/C_{TO}	32.02
X_{SO}/C_{TO}	15.3

[33, 37]

In the study of conventional characterization the total COD values were 412 ± 82.0 mg/L (298-584 mg/L) given in Table-3. The main reason of this variability is the absence of a continuous control system, although there are limit values for the wastewater to be treated in treatment plant. The results of conventional characterization and COD fraction, evaluated together show that the organic contents of influent are mostly soluble and biodegradable. This experimental study showed that inert COD amount of wastewaters changed depending on characterization of wastewater.

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