

## Determination of Kinetic Constants and Biological Treatment of Automobile Industries Wastewater

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Received 7 April 2009;

Revised 16 Aug. 2009;

Accepted 25 Aug. 2009

**ABSTRACT:** The automobile industry's wastewater not only contains high levels of suspended and total solids such as oil, grease, dyestuff, chromium, phosphate in washing products, and coloring, at various stages of chassis manufacturing but also, a significant amount of dissolved organics, resulting in high BOD or COD loads. Suspended solids can be removed from the wastewater by chemical precipitation. However, the dissolved BOD/COD compound can only be removed by biological or chemical oxidation. Effluent wastewater from the chemical sedimentation stage and the sanitary wastewaters (ratio 1:1 of sanitary to industrial feed rate) at the Bahman automobile factory was characterized and subjected to a biological treatment in a laboratory scale activated sludge unit. Experiments were conducted at different hydraulic and solid retention times. The best results were obtained with  $\theta_h=20$  h of hydraulic and  $\theta_c=20$  days of solids retention time (sludge age) resulting in an effluent COD concentration of 60 mg/Lit from an industrial feed and sanitary wastewaters of 920 mg/Lit COD content. The suspended solid content of the activated sludge effluent was approximately 57 mg/Lit. Also according to the results of experiments, kinetics constants  $k$ ,  $k_s$ ,  $k_d$ , and  $y$ , obtained (0.75, 110, 0.28 and 1.1) respectively and subsequently design equations were developed.

**Key words:** Automobile Industries, Hydraulic, Solid, Retention times, Kinetic, Constants

### INTRODUCTION

Organic compounds present in different kinds of soil and also chemicals used in the automobile industry processes cause significant organic and inorganic pollution in wastewater. Because of the high mineral content of processed materials, wastewater contains high concentrations of suspended and dissolved solids. Organic compounds present in mineral rich soil and in chemicals used for processing cause significant COD levels in the wastewater (Kozirowski and Kucharski, 1972; Nemerow, 1978; Henry and Heinke, 1989; Wahaab, 2001; Mara, 2003).

Wastewaters from different processes in the automobile industry have different characteristics. In general, the automobile industry wastewaters contain large concentrations of suspended (200-1600 mg/L) and dissolved (400-1500 mg/L) solids. COD concentration in a typical automobile

industry's wastewater is between 1000-2600 mg/L. In addition to high solids and moderate COD loads, the automobile industry wastewaters contain heavy metals such as Zinc, Nickel, Lead, Copper, Chromium and Cadmium in fairly high concentrations (El-Gohary, *et al.*, 1989; Abdel, 2000; Patterson, 1985).

Wastewater treatment is the single most important way of ensuring that sewage waste is properly handled before finally being discharged into the environmental systems (Mtethiwa *et al.*, 2008). The chemical treatment of automobile industry wastewater is commonly used for the removal of suspended solids (especially phosphorous) by chemical precipitation. However, the removal of dissolved organic compounds from the wastewater by biological treatment must be achieved, since COD removal by chemical precipitation is insufficient (Wesley Eckenfelder Jr., 2000; Benefield, and Randall, 1985; Clark *et*

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*al.*, 1977, ASCE, 1977). Effluent toxicity should also be considered as a measure of treatment efficiency in industrial wastewater treatment in addition to the standard criteria (Serkan and Fikret, 2008).

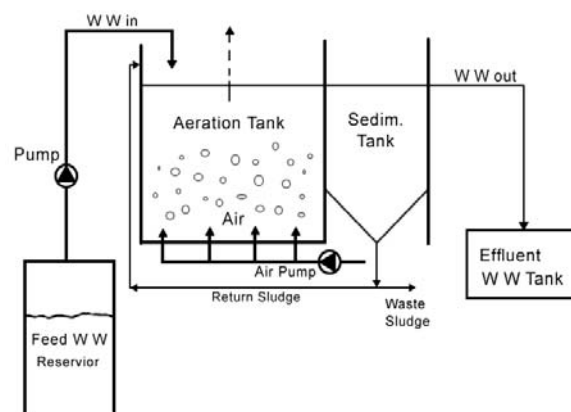
General Motors (GM) has determined the application of biotechnology for addressing environmental issues where technically applicable, and this normally represents the low cost alternative when considering both capital and operating costs over the life of a project. For the past 17 years, GM has been a leader in developing and applying innovative biological systems for in-plant treatment of contaminated water streams and end-of-pipe treatment of industrial wastewaters (Sutton and Mishra, 1997).

Historically, the major application of environmental biotechnology within GM was in the context of biological treatment of sanitary wastewaters at assembly or manufacturing plants where discharge to a municipally owned sanitary sewer was not feasible or economically attractive. In the early 1980s, a number of GM manufacturing plants adopted the use of synthetic and semi synthetic metal-working fluids versus petroleum-based products for various machining and hydraulic applications. Although there are many benefits attributed to the use of synthetics, the materials are difficult to treat in the conventional physical-chemical oily wastewater treatment flow sheet existing at most automotive manufacturing plants, giving rise to increased levels of carbonaceous biochemical oxygen demand (BOD), chemical oxygen demand (COD) and organic nitrogen compounds in the effluent. In the mid to late 1980s, GM adopted the use of the biological fluidized bed reactor system for the treatment of soluble organic carbon and nitrogen compounds (i.e., organic nitrogen and ammonia) in the effluent from existing physical-chemical treatment systems at four different manufacturing plant sites in the US (Roberts *et al.*, 2000, Sutton and Mishra, 1990). The Major objective of this study is to evaluate biological treatability of automobile industry wastewaters after chemical treatment accompanied by sanitary wastewater in equal ratio. A laboratory scale activated sludge unit was used for this purpose. The system was operated at different hydraulic residence and sludge

retention (sludge age) times to determine optimal operating conditions resulting in the best effluent quality. Experimental results were used for determination of kinetic constants to be used for design purposes.

## MATERIALS & METHODS

A laboratory scale activated sludge reactor was used for biological treatment studies. A schematic diagram of the experimental set-up is depicted in Fig. 1. Aeration and sedimentation tanks are separated by a plate and the floor of the sedimentation tank has a pyramid shape. Water flowed from the aeration to the sedimentation tank through holes on the plate and a pump is used for returning the sludge to the aeration tank. Aeration was provided by an air pump and diffusers. Wastewater was fed to the aeration tank with a desired flow rate by using a dosage pump. Since there was an operating activated sludge system for the biological treatment of automobile industry wastewater in Tehran, the inoculums culture was obtained from the wastewater treatment plant of the Bahman automobile factory, Tehran, Iran. To accomplish the laboratory experiments, the sanitary and industrial wastewater of the Bahman automobile factory was used.



**Fig. 1. A schematic diagram of the experimental set-up**

The aeration tank was filled with sanitary wastewater and inoculated with a pre-adapted culture at the beginning of continuous experiments. After one week of batch operation, the system was operated continuously. When the output of the system reached stability and the apparatus began to digest the industrial wastewater, different ratios of industrial wastewater to sanitary

wastewater was analyzed. Initially, we entered the industrial and sanitary wastewater with a ratio of 1:4 because of the existence of the complex organic compounds in the industrial wastewater. After one week with the system working under the same conditions and the acclimatization of microorganisms to new conditions, we gradually increased the mixing of the industrial and sanitary wastewater to the ratio of 1:1 (Tchobanoglous *et al.*, 2003; Reynolds, 1982; Patterson, 1985; Karia and Christian, 2006). Experiments were performed at different hydraulic residence times (10-60 h) and sludge ages (2-20 days), for at least one week, once the system reached a steady-state. The hydraulic residence time and sludge age were adjusted by changing the feed flow rate and by the daily removal of sludge from the sedimentation tank, respectively. Feed and effluent samples were centrifuged and COD, total nitrogen and total phosphate analysis were done on clear supernatants by using the Standard Methods (Greenberg *et al.*, 2001). Total suspended solids were determined by filtering samples from 0.45µ Millipore filter and determining the weight of solids on the filter paper after drying to constant weight.

## RESULTS & DISCUSSION

Effluent wastewater at the chemical precipitation stage was obtained from the Bahman automobile factory, Tehran, Iran and analyzed in laboratory. Average values of analyses performed at different times are presented in Table 1. The characterization of the raw wastewater is presented in Table 2.

The biological treatment of chemically treated wastewater and sanitary wastewater (ratio 1:1) was accomplished in an activated sludge unit. The wastewater was fed to the aeration tank and clear effluent was removed from the sedimentation tank. The system was operated at different hydraulic and sludge retention times.

**Table 1. Characterization of the effluent wastewater from chemical treatment**

COD (mg/L)	BOD (mg/L)	TN (mg/L)	TP (mg/L)	TSS (mg/L)	pH
870	360	5	10	700	8.1

In order to investigate the effect of hydraulic residence time ( $\theta_H$ ) on the COD removal performance, the system was operated at different  $\theta_H$  values (10-60 h) at a constant sludge age of  $\theta_c = 10$  days. Experimental results obtained at a steady-state are summarized in Table 3. Effluent COD decreased from 250 mg/L at  $\theta_H = 10$  h to 115 mg/L at  $\theta_H = 48$  h. Effluent suspended solids concentration was around 60 mg/L at all hydraulic residence times. Hydraulic residence time should be around  $\theta_H = 40-50$  h at a sludge age of  $\theta_c = 10$  days in order to obtain high effluent quality.

The effect of sludge age on system performance was investigated by changing the sludge age between  $\theta_c = 2-20$  days at constant hydraulic residence time of  $\theta_H = 20$  h. The Results of this set of experiments are presented in Table 4. Effluent COD decreased from 320 mg/L at  $\theta_c = 2$  days to 60 mg/L at  $\theta_c = 20$  days. Total suspended solids (TSS) varied between 55 to 65 mg/L and the pH between 7.1 and 7.8 in the effluent. The effluent quality was acceptable for sludge age values larger than 10 days. The optimal operating conditions were  $\theta_c = 20$  days and  $\theta_H = 20$  h at optimum pH=7.2 and T= 27 °C resulting in an effluent COD of 60 mg/L.

Experimental data obtained at different sludge ages (Table 4) were used to determine kinetic constants of the system. Activated sludge design equations used for this purpose are given below (Tchobanoglous *et al.*, 2003; Qasim, 1999; Droste, 1996; Lin, 2001):

$$U = \frac{1}{X} \frac{dS}{dt} = \frac{S_0 - S}{\theta_H \cdot X} = \frac{k \cdot S}{k_s + S} \quad (1)$$

**Table 2. Characterization of raw wastewater**

	COD(mg/L)	BOD(mg/L)	TN(mg/L)	TP(mg/L)	TSS(mg/L)	pH
<b>Industrial</b>	2700	730	25	250	1470	8.1
<b>Sanitary</b>	980	490	65	11.5	300	6.8

**Table 3. Variation of COD removal efficiency with hydraulic residence time  $\theta_c = 10$  days,  $T_{Ave} = 27$  °C)**

$\theta_H$ (h)	COD <sub>0</sub> (mg/L)	COD <sub>e</sub> (mg/L)	Biomass(mg/L)	TSS <sub>e</sub> (mg/L)	T °C	pH	E (%)
10	1080	250	2240	65	26	7.2	76.85
16	985	200	2762	-	27	7.3	79.70
20	915	160	2725	60	28	7.4	82.51
30	880	150	2790	-	30	7.21	82.95
35	960	130	2817	56	27	7.6	86.46
48	960	115	3273	60	27	7.8	88.02
60	1010	130	3115	46	26	7.8	87.13

**Table 4. Variation of effluent quality with different sludge age ( $\theta_H = 20$  h,  $T_{Ave} = 27$  °C)**

$\theta_c$ (days)	COD <sub>0</sub> (mg/L)	COD <sub>e</sub> (mg/L)	Biomass (mg/L)	TSS <sub>e</sub> (mg/L)	T °C	pH	E (%)
2	880	320	980	-	28	7.1	63.64
5	960	190	1960	56	26	7.2	80.21
8	960	180	2240	65	26	7.2	81.25
10	960	120	2650	54	27	7.8	87.50
15	915	75	3520	61	29	7.6	91.80
20	920	60	3650	57	27	7.2	93.48

or

$$\frac{1}{U} = \frac{\theta_H \cdot X}{S_0 - S} = \frac{1}{k} + \frac{k_s}{k} \frac{1}{S} \quad (2)$$

Where  $U$  is specific rate of COD removal (mg COD/mg  $X$  days);  $k$  is maximum COD removal rate constant (per day);  $K_s$  is saturation constant (mg/L);  $X$  is biomass concentration in aeration tank (mg/L);  $S_0$  and  $S$  are feed and effluent COD (mg/L). Definition of the sludge age results in the following equation:

$$\frac{1}{\theta_c} = \mu = Y \frac{k \cdot S}{k_s + S} - k_d = YU - k_d \quad (3)$$

Where  $Y$  is the growth yield coefficient (mg  $X$ /mg COD), and  $k_d$  is the death rate coefficient (per day).

Experimental data presented in Table 4 was plotted in form of  $1/U$  versus  $1/S$  as shown in Fig. 2. From the slope and intercept of the best-fit data the following values were found for the constants:

$$k = 0.75 \text{ per day} \quad K_s = 110 \text{ mg/L}$$

Similarly, the experimental data was plotted in form of  $1/\theta_c$ , versus  $U$  as shown in Fig. 3. From

the slope and intercept of the best-fit data the following values were found for  $Y$  and  $k_d$ :

$$Y = 1.1 \text{ mg } X/\text{mg COD} \quad k_d = 0.28/\text{day}$$

The high value of the yield coefficient ( $Y$ ) may be result of error in biomass concentration measurements due to high suspended solids content of the wastewater.

By using the kinetic constants, design equations may be written as follows:

$$S = \frac{k_s(1 + k_d\theta_c)}{\theta_c(Yk - k_d) - 1} = \frac{110(1 + 0.28\theta_c)}{.825\theta_c - 1}, \quad (4)$$

and

$$X = \frac{Y(S_0 - S)\theta_c}{(1 + k_d\theta_c)\theta_H} = \frac{1.1(S_0 - S)\theta_c}{(1 + 0.28\theta_c)\theta_H} \quad (5)$$

## CONCLUSIONS

The automobile industry wastewater from the chemical preci-pitation stage and the sanitary wastewater were characterized and subjected to bio-logical treatment in a laboratory scale activated sludge unit. The effects of important process variables such as hydraulic residence and sludge age (solids retention time) on COD removal

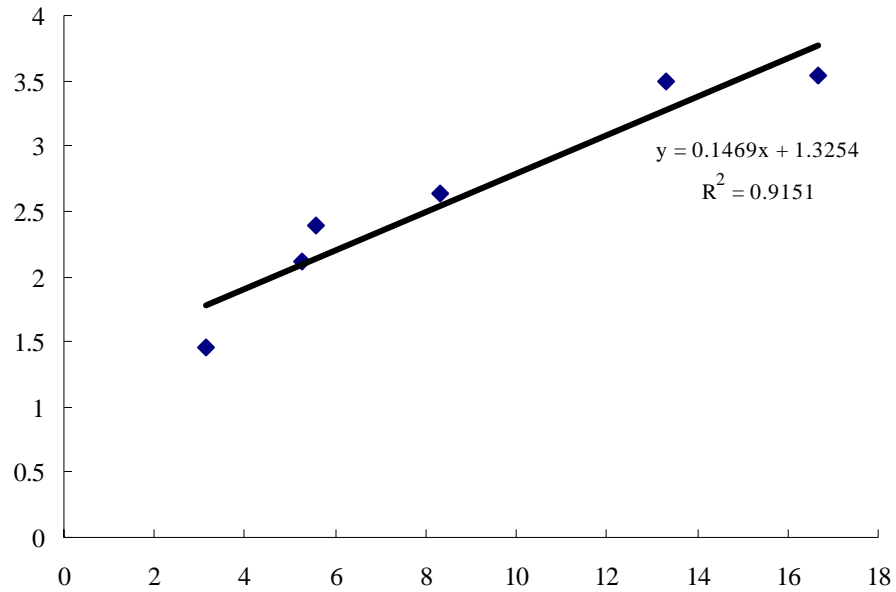


Fig. 2. Form of experimental data of  $1/U$  versus  $1/S$

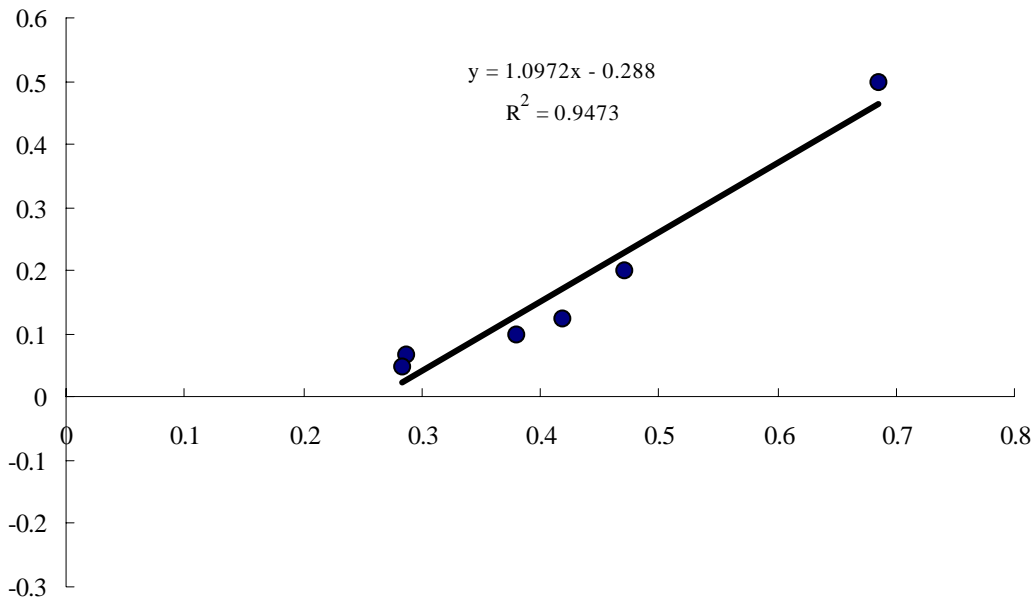


Fig. 3. Form of experimental data of  $1/\theta_c$  versus  $U$

performance of the system were investigated. The effluent COD decreased with increasing hydraulic and solids retention times. The best effluent quality was obtained at 20 h of hydraulic and 20 days of solids retention resulting in  $COD_e = 60$  mg/L and  $TSS_e = 57$  mg/L.

Experimental data was used to determine kinetic and stoichiometric constants of the system and design equations were developed.

#### LIST OF SYMBOLS

- $k_d$  death rate constant for organisms (per day)
- $k$  maximum COD removal rate constant (per day)
- $K_s$  saturation constant (mg/L)
- $S_o, S$  COD in the feed and effluent (mg/L)
- $TS$  total solids concentration (mg/L)
- $TSS$  total suspended solids concentration (mg/L)
- $U$  specific rate of COD removal (mg COD/mg X day)

$X$	biomass concentration in aeration tank (mg/l)
$Y$	growth yield coefficient for organisms (mg X/mg COD)
$\theta_H$	hydraulic residence time (h)
$\theta_C$	sludge age or solids retention time (days)
$\mu$	specific growth rate of organisms ( $\text{h}^{-1}$ )

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