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ANALYTICAL MODELLING OF ORGANIC CONTAMINANTS IN LEACHATE*

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Mathematical modelling is a helpful tool for predicting the hazards which arise from contaminants in leachate. These kinds of models are based on exponentially varying leachate concentration with time. In this research, a model for estimating the concentration of organics, measured as Chemical Oxygen Demand (COD), in leachates from solid waste disposal areas is developed. The model contains processes such as dissolution/dilution, mass transfer, substrate utilization, and microbial mass production. The recommended analytical model is compared with experimental data from two laboratory-scale plants. In addition, the variations of model parameters with the governing processes are determined with respect to time. Experimental data from laboratory and field studies in literature is simulated to verify the model. In order to determine some estimated parameters found by trial and error during modelling, multiple regression equations for the values from simulations are created.

Key Words—Landfills, leachate, mathematical modelling, organics, COD, seasonal wastes.

1. Introduction

Leachate formation by the movement of moisture through landfilled solid wastes may be an important source of groundwater pollution. Leachates overloaded with various contaminants can be controlled by several measures. Control measures in a landfill can reduce the problem, but do not remove it completely. There are two general measures: collection of leachate for treatment; and the attenuation of pollutants through the soil layer above the water table. The selection of the most appropriate treatment is difficult due to the variation in leachate quality with landfill age. Knowledge of leachate quantity and quality should be gained for the control and treatment of leachate.

Efforts towards the solution of the problem have been increased in recent decades. Most studies are based on the experimental simulation of leaching in pilot plants. Several studies have estimated the behaviour of leachate by comparing the observed results from pilot plants set up in the laboratory and field with those obtained from mathematical models. All mathematical expressions proposed by previous investigators are empirically based on an exponential function of time, because each expression is based on experimental data obtained from an original pilot plant. The application of these empirical expressions may supply values close to actual conditions by making some simplifications which are often unrealistic and lack theoretical backing. In a recent mathematical modelling applied to inorganic and organic leachate by Straub & Lynch (1982), more reasonable simulations with several experimental results from the literature were submitted. Their studies are based on simple, well mixed single reactor concepts,

* A companion paper on modelling inorganic contaminants in leachates is in preparation and planned to be published in a later issue of *Waste Management and Research.*

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and on unsaturated flow of moisture, contaminant generation and transport in porous media. The study of the single reactor model proposed by Straub and Lynch needs some analytical improvements, but is used as a guide in this paper.

In the present study, a model proposed for predicting concentrations of organic pollutant in leachate is calibrated with the results obtained from pilot plants constructed in the laboratory. Major properties of the model such as parameters dealing with mechanisms of mass transfer, dilution and biological transformations are investigated. After using verification examples from literature of laboratory and field experimental data, some estimated parameters used in simulations are regressed using the least squares method to obtain statistically meaningful relationships.

2. Mathematical model

The mathematical model is based on the following assumptions: constituents of solid wastes are mixed uniformly in a column having a volume V(1); the waste mass in the column is mixed uniformly and has the moisture content of θ ($\mathrm{cm^3\,cm^{-3}}$); the pollutant concentration is C ($\mathrm{mg\,l^{-1}}$) and the microorganism concentration is X ($\mathrm{mg\,l^{-1}}$). The pollutant and microorganisms are also uniformly distributed. The upflow of decomposition gas formed from organic materials, low flow rate of moisture, and well mixed contents of materials are some factors affecting the uniformity of distribution in the column. At the start of leaching, materials reach the field moisture capacity of θ_f ($\mathrm{cm^3\,cm^{-3}}$) and after that, a steady state for input/output in the column is reached (i.e. $Q_i = Q$). The model neglects the physical variations resulting from settling occurring in the course of time, as well as the ratio of wastes which can be transformed into gas from leachable wastes. In the prediction of leachate concentration, the dilution, mass transfer and biological decomposition are the essential factors. Also, growth rate of microorganisms which occur through the decomposition process is taken into account in the model. The experimental column used was regarded as air tight and filled with highly decomposable organic waste material, consequently, the medium in the column was modelled as a fully anaerobic medium.

Based upon the above assumptions, the governing equation of this model can be written as:

$$\frac{d(CV\theta)}{dt} = C_iQ_i - CQ + V\theta(R + R_1 + R_2) \tag{1}$$

where: Q_i and Q are influent and effluent flowrates ($\mathrm{mm\,m^{-2}\,day^{-1}}$ or $\mathrm{l\,m^{-2}\,day^{-1}}$)*; C_i and C are contaminant concentrations in input and output flows ($\mathrm{mg\,l^{-1}}$; R is the mass transfer rate ($\mathrm{mg\,l^{-1}\,day^{-1}}$); R_1 is the substrate utilization rate ($\mathrm{mg\,l^{-1}\,day^{-1}}$); and R_2 is the microorganism growth rate ($\mathrm{mg\,l^{-1}\,day^{-1}}$).

Ignoring the contaminant concentration of the input flow (i.e. taking $C_i = 0$) simplifies equation 1:

$$\frac{dC}{dt} + \frac{CQ}{V\theta} = R + R_1 + R_2 \tag{2}$$

* This unit is regarded as equivalent to the unit $\mathrm{l\,m^{-2}\,day^{-1}}$ since it describes the depth of precipitation at each $\mathrm{m^2}$ of surface area.

A solution to equation 2 can be expressed as:

$$C(t)=Exp[-G(\bar{t})]\{C_o+\int_{t=0}^{t}(R+R_1+R_2)ExpG(\bar{t})dt\} \tag{3}$$

where:

$$G(\bar{t})=A\int_{\bar{t}=0}^{\bar{t}}\frac{Q(\bar{t})}{V\theta_f}d\bar{t} \tag{4}$$

is an expression dealing with cumulative precipitation. $\bar{t}$ is a dummy integration variable and C_o is initial contaminant concentration (mg l^{-1}).

This analytical solution (equation 3) allows for simulation with contaminants having different characteristics for both mass transfer and biological transformation mechanism. For instance, there is no mass transfer from the start of leaching for highly water soluble organic compounds, that is $R=0$. However, organic constituents dissolved in the course of time have a variable $R(t)$. R mass transfer rate varies with time due to decrease in leachable matter with time. On the other hand, the leaching characteristics of each group of materials in waste also show variation with time. Waste materials such as kitchen, garden, and outdoor market wastes can pass into leachate in a short time, whereas those such as paper and textiles take much longer.

The second part consisting of organics, such as textile and paper, is ignored in the model because of the negligible initial transfer rate. Therefore, total mass transfer rate is assumed to consist of the first part of rapidly degradable organics only:

$$R(t)=k\frac{S(t)}{S_o}[C_{\max}-C(t)] \tag{5}$$

where: k is the coefficient of the mass transfer rate (day^{-1}); S_o is initially present leachable solids (kg); $S(t)$ is leachable solids at time t (kg); and $C_{\max}$ is observed maximum contaminant concentration (mg l^{-1}).

The mass transfer of organics passed into water and decomposed by existing microorganisms is estimated at the following rate:

$$R_1(t)=\frac{\mu_m X(t)C(t)}{Y[K_s+C(t)]} \tag{6}$$

and besides, the part of organics used for the growth of microorganisms can be expressed as:

$$R_2(t)=-YR_1(t)-k_dX(t) \tag{7}$$

where: μ_m is the maximum specific growth rate (day^{-1}); Y is the maximum yield coefficient (mg mg^{-1}); K_s is the half velocity constant (mg l^{-1}); and k_d is the endogenous decay coefficient (day^{-1}).

The microorganism concentration in the column is expressed as:

$$X(t)=Y\frac{C_o^*(t)-C(t)}{1+k_dT} \tag{8}$$

where: $C_o^*(t)$ is the concentration of substrate which can be decomposed at time t (mg l^{-1}); $C(t)$ is the concentration of substrate which is actually at time t (mg l^{-1}); and T

is the average hydraulic retention time (day) that is determined by dividing the total void volume with the average water application rate.

For this model, there are four different situations:

Case 1: For organics which are both readily biodegradable and dissolvable

$$C(t) = Exp[-G(\bar{t})]\{C_o + \oint(R_1 + R_2)ExpG(\bar{t})dt\} \tag{9}$$

Case 2: For organics which are readily biodegradable but not easily dissolvable

$$C(t) = Exp[-G(\bar{t})]\{C_o + \oint(R + R_1 + R_2)ExpG(\bar{t})dt\} \tag{10}$$

Case 3: For organics which are not biodegradable but readily dissolvable

$$C(t) = C_o Exp[-G(\bar{t})] \tag{11}$$

Case 4: For organics which are neither biodegradable or dissolvable

$$C(t) = Exp[-G(\bar{t})]\{C_o + \oint RExpG(\bar{t})dt\} \tag{12}$$

In the present study, we examine only the second case, in which the experimental data (as COD) is obtained from two pilot plants with domestic solid waste, constructed in the laboratory.

3. Experimental

In order to compare the model using experimental data in the laboratory, two simulated landfills containing waste samples with different characteristics (Basturk 1980) were constructed, and experiments were carried out for nearly 1 year. These filled columns comprised of plexiglass columns 0.30 m in diameter and 1 m in height. The mixtures of wastes were obtained by grinding each waste material group one by one in a coarse grinder (diameter $\leq$ 2 cm) and mixing completely. The mixtures were packed in the columns. The first waste mixture was at a height of 0.75 m and weight of 46 kg, and the second waste mixture was at a height of 0.70 m and weight of 35 kg. Their moisture contents were determined by oven drying at 105°C for 48 hours, as 40.1 and 26.8%, respectively.

After settling down, to prevent air entry into columns they were sealed and several measures were taken from the influent and effluent ports. Before the start the normal water applications, field moisture capacities (θ_f) of mixtures were determined by rapid water application, as 0.526 and 0.454 $cm^3 cm^{-3}$, for summer and winter wastes, respectively. The initial moisture contents of raw mixtures were also taken into account. Water application was carried out daily according to local meteorological observations of 50 years by means of a uniform perforated tray inside the columns.

The leachate samples were collected in containers of 2.5 l stored at 3–5°C until analysed, and were analysed for COD in accordance with Standard Methods used (1985).

4. The estimating of model parameters

The hydraulic retention time in each column was calculated to be 210 and 169 days by

$$T=\frac{V\theta_f}{Q} \tag{13}$$

where Q is the average flow rate (mm m^{-2} day^{-1}).

To determine the coefficient of mass transfer rate (k) from equation 5, R values can be estimated by the following expression:

$$R=\frac{C^*}{T} \tag{14}$$

where C^* is the average contaminant concentrations (mg l^{-1}) which has been observed during 1–2 decades of observation of leaching processes. In this calculation, C^* is taken as 10 000 mg l^{-1} by collating the typical COD values in literature. Hence, approximate R values are calculated as 50 and 60 mg l^{-1} day^{-1}, respectively. Then by equation 5, k values are obtained as approximately 0.003 day^{-1} for both wastes. In order to determine the biological decomposition situation during the leaching process, it is assumed that: $Y=0.04$ mg mg^{-1}; $\mu_m=0.036$ day^{-1}; $K_s=5000$ mg l^{-1}; $k_d=0.01$ day^{-1}; and the initial microorganism concentration $(X_o)=2$ mg l^{-1}.

5. Application of the model

The simulations obtained are shown in Fig. 1. In these simulation studies for wastes in summer and winter, the k value of 0.003 day^{-1} is used, and by the selection of an appropriate initial (C_o) and maximum ($C_{\max}$) contaminant concentration, good simulated curves which vary according to the amounts of seasonal moisture are obtained. The best simulated curves are ensured for $C_o=C_{max}=60\,000$ mg l^{-1} in the summer column and for $C_o=C_{max}=50\,000$ mg l^{-1} in the winter column.

The COD paramater is regarded as a suitable general pollutant parameter to simulate the organics which pass into water in the course of time because the simulation curves are in close agreement with values obtained from pilot plant data. In addition, it is shown that the composition of waste affects the selection of the values of C_o and C_{max}.

The estimation of the model for variations in pollutant concentration with and without microorganisms, and microorganism concentrations during a period of 10 years are plotted in Fig. 2. Mass transfer and biological transformation rates which affected the determination of pollutant concentration over a period of 10 years are examined in Fig. 3.

The microorganism concentration begins to increase after the 600th day. However, it only reaches its maximum value after almost 3 years. After this, increase and decrease in the microorganism concentrations are due to seasonal conditions. Obviously, high microorganism concentrations are caused by high substrate concentrations during arid seasons. In rainy seasons, the substrate concentration substantially decreases due to high infiltration rates as does the microorganism concentration in the media. Moreover, during winter the endogenous respiration also reduces the decomposition process.

The concentration of organic matter decreases gradually during the 10 years, as well as being affected by variations in rainfall. In the absence of toxic compounds in the

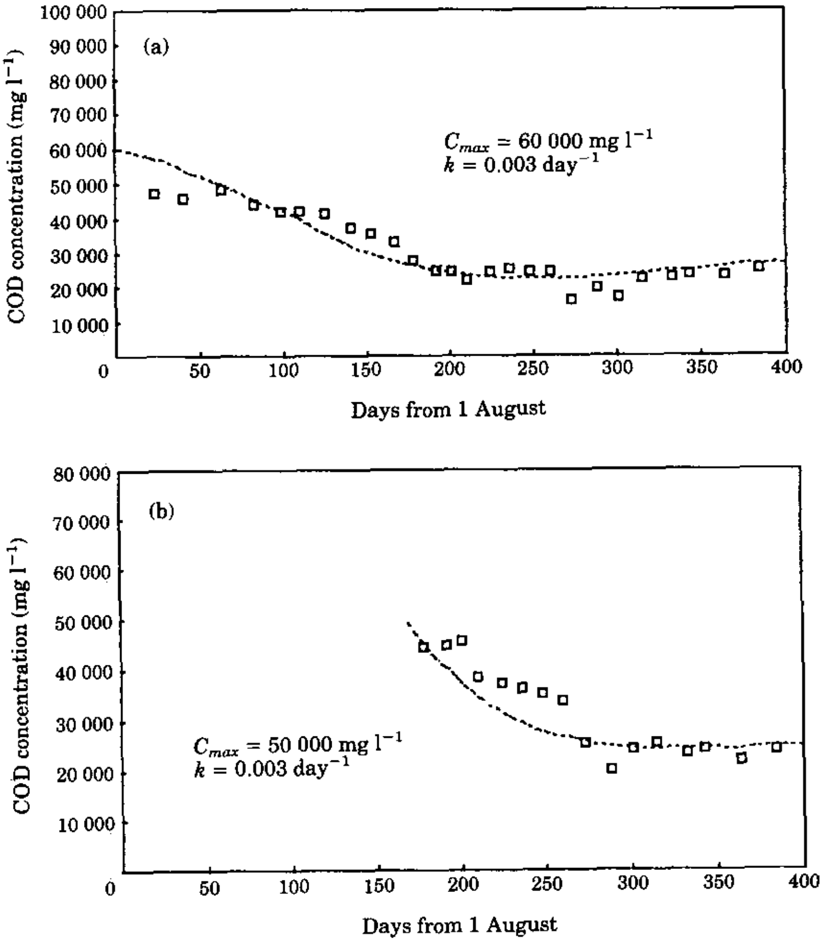

Fig. 1. The simulation of COD data observed for a) summer waste and b) winter waste. (□) experimental; (....) model.

media, while the microorganism concentration is high, the decrease in organic matter concentration (C_l) in the leachate is much higher. Also, the decreasing rate of nontoxic organic matter concentration (C_l) gradually drops from the maximum microorganism concentration (from about 3 years), and then remains at very low values. However, if toxic matters exist in the solid waste mixture, the media may behave as if there are no microorganisms. Consequently, organics in the presence of toxic compounds can be regarded as behaving like organic matter, and their concentration, C decreases at a much lower rate compared to C_l.

The rate of mass transfer, R increases very quickly from the beginning of the leaching, and reaches a maximum value at the end of the first year. After that, it begins to decrease due to loss of leachable matter. This parameter has tendencies to decrease or increase depending on the infiltration rates. Since the microorganism concentration is very low during the first 600 days, R becomes a dominant factor in the media. At the end of the period of 600 days, the substrate utilization rate, R_l is more affected by seasonal variations than R. This is related to the availability of sufficient substrate for the

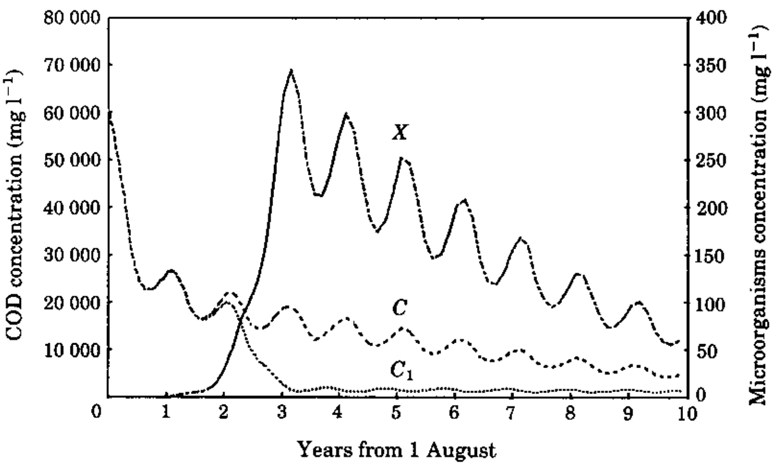

Fig. 2. Variation of pollutant and microorganism concentration during a 10 year period.

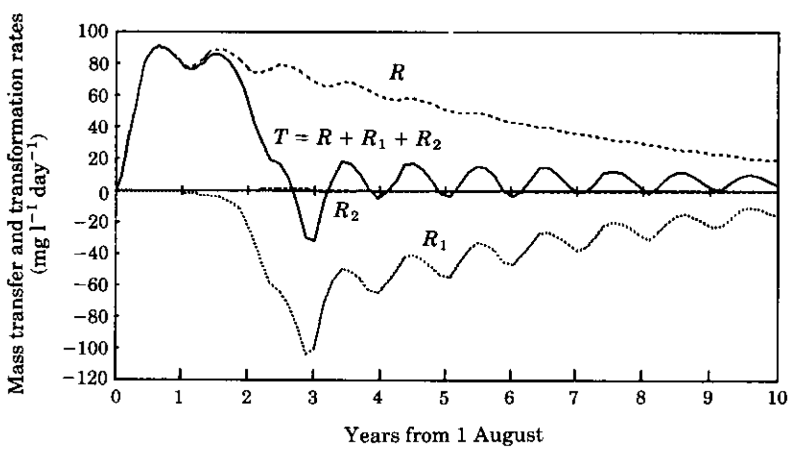

Fig. 3. Variation in rates of mass transfer and biological transformation affecting the determination of pollutant concentration.

microorganisms. Microorganism growth rate, R_2 increases a little during winter, and in the arid periods endogenous respiration occurs. R_2 is not an important factor in the overall process. Furthermore, the endogenous respiration dominates in the media after 4 years because of considerable decrease in the amount of existing substrate.

Some experimental data from laboratory and field pilot test plants in the literature (Pohland 1975, Barber & Maris 1984 and Leckie *et al.* 1979) were simulated using the variables shown in Table 1. Microbiological decomposition parameters were taken to be the same as those used in the previous simulations. The data from pilot plants, despite varying in a wide range of the installation features, all fitted rather well, as shown in the simulation curves in Figs 4 to 6.

In this study, it was found from the simulation results of five sets of experimental laboratory data and the literature that some simulation parameters, such as the maximum concentration (C_{max}) and the mass transfer rate coefficient (k), provided good

TABLE 1
Variables used for the simulation of experimental data (COD) from several studies in literature

Variable	Unit	Pohland (1975)	Barber & Maris (1984)	Leckie *et al.* (1979)
V, volume	l	2000	2.72×10^7	7.5×10^5
θ_f, field capacity	cm cm^{-1}	0.471	0.550	0.500
A, cross sectional area	m^2	0.658	6817	225
S_o, leachable solids	kg	158.5	2.16×10^6	8.8×10^4
T, average retention time	day	167	980	195
k, mass transfer rate coefficient	day^{-1}	0.001	0.003	0.005
C_o, initial concentration	mg l^{-1}	18,100	90,000	28,000
C_{max}, maximum concentration	mg l^{-1}	30,000	90,000	40,000
Q, daily mean flow rate	mm day^{-1} m^{-2}	5.641	2.240	8.550
D_d, dry density	kg m^{-3}	317	600	466
H, waste height	m	3.07	4.00	3.07
γ_1, the ratio of leachable matter	%	25.0	20.0	18.6
X_o, initial microorganism conc.	mg l^{-1}	20	2	2

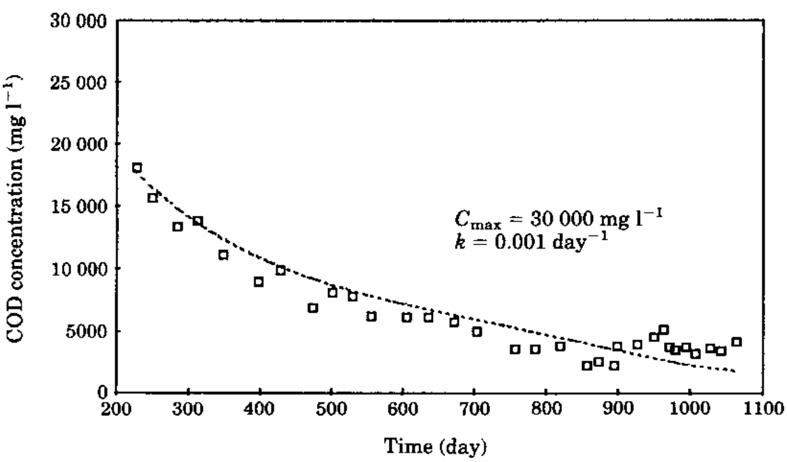

Fig. 4. The simulation of laboratory COD data from Pohland (1975). (□) experimental; (....) model.

agreement with the modelling approach. These parameters all depend substantially on the ratio of the initially present leachable matter amount (γ_1) and the dry density of the mass installed (D_d). Multiple regressions were used to identify the statistical relationships among the variables. The following equations were obtained:

$$k = 1.993\times10^{-3} + 5.155\times10^{-6}\times D_d - 7.857\times10^{-5}\times\gamma_l \quad (15)$$

$$C_{max} = -97\,810 + 247.4\times D_d + 1829.3\times\gamma_l \quad (16)$$

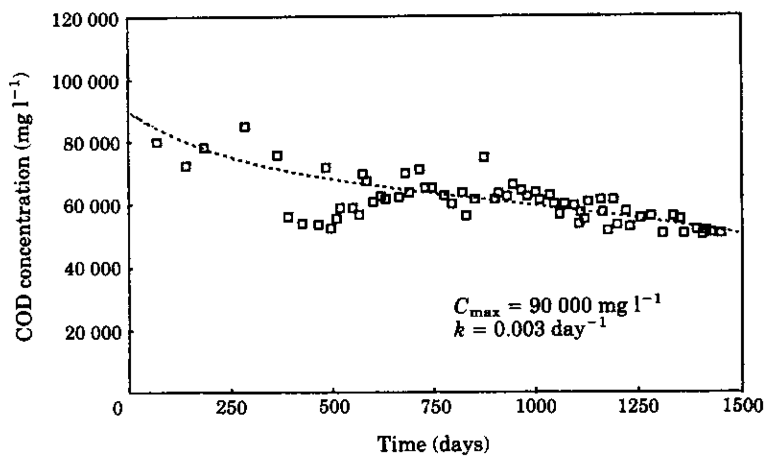

Fig. 5. The simulation of field COD data from Barber & Maris (1984). (□) experimental; (....) model.

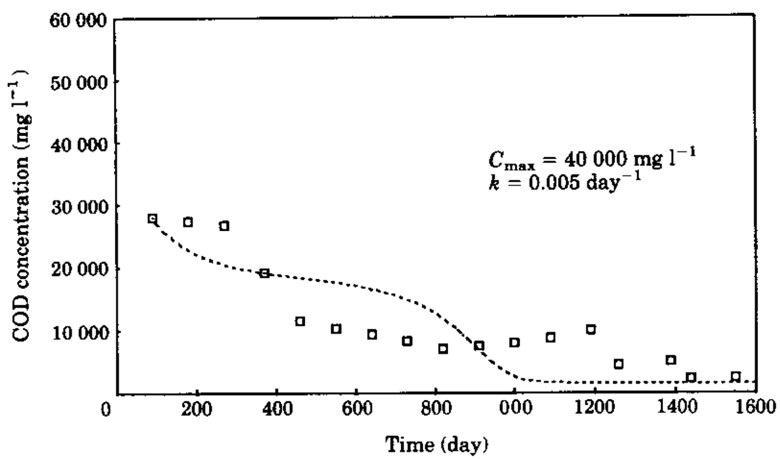

Fig. 6. The simulation of field COD data from Leckie *et al.* (1979). (□) experimental; (....) model.

6. Conclusions

The application of the present model, for the parameter of COD, gives good simulation curves. The concentration values from simulations are affected not only by physical size of the waste mass and the rate of water application, but also by chemical features of the waste mixtures.

During the application of the desired model over the long term, it was observed that the concentrations of contaminant and microorganisms are both affected by seasonal rainfall differences. Furthermore, the long term variations in rates of mass transfer and biological decomposition (i.e. substrate utilization and microbial growth) that were effective in the determination of contaminant concentration were studied. The effect of different infiltration rates resulting from seasonal changes in rainfall and substrate reduction in the experimental columns were also studied.

Finally, the equations obtained from multiple regression analyses were found to provide good approximations of the variations in COD concentrations over time. The observed results from experimentation were similar to the estimated values for five calculated simulations.

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