Kinetic modelling of degradation of phenolic compounds in leachate

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Abstract

Leachates from municipal solid waste (MSW) contain a large number of compounds many of which are not hazardous to health and nature as they represent degradation products ranging from small volatile acids to refractory fulvic and humic-like compounds and some of which are hazardous compounds including aromatic compounds, halogenated compounds, phenolic compounds, pesticides, heavy metals, and ammonium. Phenolic compounds released into the environment are of high concern because of their potential toxicity. These compounds found in the leachate include phenol, cresols and substituted and chlorinated phenols that have been designated as priority pollutants by the U.S. Environmental Protection Agency. Phenolic compounds degrade under anaerobic conditions in landfill sites. In this study, the degradation of phenolic compounds in leachate has been investigated by using leachate recirculated anaerobic reactors representing bioreactor landfills. Wastes representing Istanbul municipal solid wastes were disposed in the reactors. Phenolic compounds of leachate are analyzed by using Gas Chromatograph. Before injection of leachate to the Chromatograph, contaminants in the leachate are extracted by using solid phase micro extraction (SPME) method. A first-order kinetic model was adopted to represent the microbial degradation of phenolic compounds under anaerobic conditions.

Keywords: modelling, leachate, phenolic compounds, degradation.

1 Introduction

Wastewater flow through municipal solid wastes disposed at landfill sites and removal of soluble compounds by the non-uniform and intermittent percolation of water through the refuse mass result in the production of leachate. Leachate

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may be characterized as a water-based solution of four groups of pollutants such as dissolved organic matter, inorganic macro components, heavy metals, and xenobiotic organic compounds [1, 2]. Additionally landfill leachate contain a large number of hazardous compounds, including aromatics, halogenated compounds, phenols, pesticides, heavy metals, and ammonium, which can be assumed to be hazardous even in small amounts and their detrimental effects are often caused by multiple and synergistic effects [3–6]. Particularly, phenolic compounds released into the environment are of high concern because of their potential toxicity. These compounds found in the leachate include phenol, cresols and substituted and chlorinated phenols. Phenol, cresols, short-chain phenols previously reported in leachates of municipal and industrial landfills [7, 8] may originate from different types of wastes. Phenol and substituted phenols are common transformation products of several pesticides. Many substituted phenols, including chlorophenols, nitrophenols, and cresols, have been designated as priority toxic pollutants by the U.S. E.P.A. [9].

In conventional landfills, waste degrades via fermentation processes under anaerobic conditions. Anaerobic degradation in conventional landfills occurs as a consequence of a series of metabolic interactions among various groups of microorganisms. As other organic constituents of the leachate, phenolic compounds degrade under anaerobic conditions. The metabolic pathway for phenol degradation under anaerobic conditions is by reduction and also via benzoic acid [9]. Degradation of phenols by anaerobic consortia under asetogenic and methanogenic conditions has been reported by many researchers [9–17].

In this study, first-order kinetic model was adopted to degradation of fourteen different phenolic compounds (phenol, 2-Chlorophenol (2-CP), 2-Metilphenol (2-MP), 3-Metilphenol (3-MP), 4-Metilphenol (4-MP), 2-Nitrophenol (2-NP), 4-Nitrophenol (4-NP), 2,4-Dinitrophenol (2,4-DNP), 2,4-Dichloropenol (2,4-DCP), 2,6-Dichloropenol (2,6-DCP), 2,4,5-Trichlorophenol (2,4,5-TCP), 2,4,6-Trichlorophenol (2,4,6-TCP), 2,3,4,6-Tetrachlorophenol (2,3,4,6-TeCP), Pentachlorophenol (PCP)) to represent the microbial degradation of phenolic compounds under anaerobic conditions.

2 Materials and methods

A pilot-scale landfill reactor was simultaneously run for a period of about 540 days to investigate the anaerobic degradation of phenolic compounds in leachate. The reactor was made of HDPE pressurized pipe with a wall thickness of 5 mm. The diameter (DR), height (HR), effective volume (VE) and total volume (VT) of the reactor were 40 cm, 250 cm, 0.201 m^3 and 0.251 m^3, respectively. The bottom of the reactor consisted of a 15-cm gravel drainage with a perforated pipe (2.5 cm diameter) inserted to collect and to discharge the generated leachate.

The reactor was operated by recirculation of leachate to represent bioreactor landfills. The leachate collection was performed by opening the discharge valve on a daily-basis at the beginning of the experiment, and at 1 or 2 week intervals for the following periods. The discharged leachate from the reactor was stored to

use for recirculation. Landfill gas was collected via the perforated pipes, which was located in the center of the reactor (4 cm diameter and 170 cm height). Temperature probes were also located at 120 cm depths from the top of the waste to measure temperature variation in the landfill reactor. Schmeatic view of landfill bioreactor is given in fig. 1.

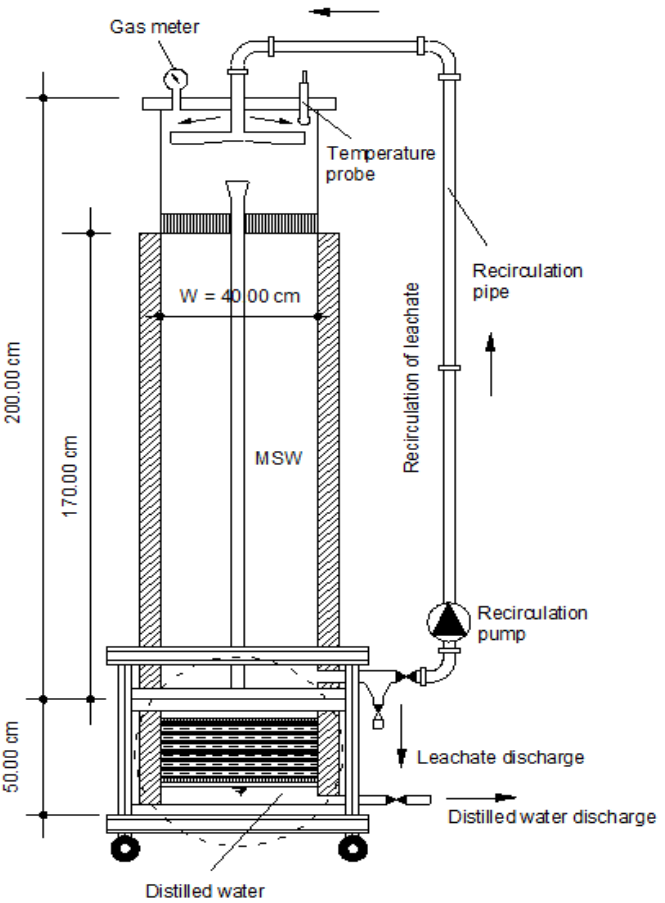

Figure 1: Schematic view of landfill bioreactor.

The disposed municipal solid wastes in the landfill reactor were obtained from the Odayeri Sanitary Landfill (41°14'8"N, 28°51'16"E) in Istanbul, Turkey. The average composition of solid waste samples collected from Odayeri Sanitary Landfill was 44% organic, 8% paper, 6% glass, 6% metals, 5% plastic, 5% textile, 9% nylon, 8% diaper, and 9% ash and others [18]. The reactor was filled with approximately 150 kg of fresh MSW.

To determine phenol and phenolic compounds in leachate, SPME method is used as conducted by Ribeiro *et al.* [19]. 85 μm polyacrylate fiber (from

SUPELCO), a SPME fiber holder (from SUPELCO) and (0.25 mm x 30 m x 0.25 μm) column are used for this method. The fiber was conditioned in the GC injector for 1 h at 250°C. The vial capacity was 4 mL, handling 2 mL of sample. The temperature and stirring velocity (750 rpm) were controlled during extraction. The pH of the samples were adjusted (pH < 2) with H_2SO_4 by using pH meter (Jenway 3040 Ion Analyser) and a pH probe (HI1230, Hanna Instruments). Na_2SO_4 was used to saturate samples. GC/FID analyses were carried out using a Varian 3900 Model GC/FID Gas Chromatograph with the helium carrier gas at 10 mL/min. Injector and detector temperatures are 250 and 320°C, respectively. The temperature program is increased to 280°C at a heating rate of 6°C/min and held at this temperature for 5 min. Phenolic compounds are quantified by peak area using external standard method. Quantification is achieved using peak area calculations, and compound identification is partly carried out using correlations between retention times. EPA 8040A and EPA 8040B phenol calibration mixtures (from SUPELCO) containing eighteen phenols with an individual concentration of 2000 μg/L in isopropyl alcohol was used to obtain fourteen phenol derivatives.

3 Results and discussion

At the beginning of the operation, phenol concentration in the reactor was determined as 12.7 μg/L. After approximately 200 days of anaerobic landfilling, phenol concentration in this reactor reached maximum value because of the reduction and decomposition of the phenolic compounds in leachate. Maximum value of phenol concentration in the reactor was determined to be about 195 μg/L. Phenol concentration decreased after reaching maximum value because of phenol degradation in anaerobic medium oppositely to the increasing trend in first 200 days. Phenol concentration in the reactor was determined to be 32 μg/L after approximately 400 days of operation, and no considerable change was observed till the end of the study.

2-CP concentration in the reactor was almost in the range of 200-300 μg/L at the beginning of the landfilling operation. The concentration first reached its maximum value rapidly after 100 days of operation, and decreased from 490 μg/L below 20 μg/L after 400 days of operation. Results indicated that no considerable change was recorded in leachate samples from 400 days of operation to the end of the study. Our results showed that that 2-CP could be degrade anaerobically. This result is consistent with Armenante *et al.* [20] who indicated that both monochlorophenols and more heavily chlorinated phenols can be degraded under anaerobic conditions. Degradation of chlorinated phenols under anaerobic conditions has been studied by several researchers [21–24].

At the beginning of the study, 2-MP concentrations of the reactor was determined to be about 6 μg/L. After reaching maximum value, 2-MP concentrations decreased because of the degradation. Maximum 3-MP and 4-MP concentrations in the reactor was determined as 14.4 and 16.8 μg/L, respectively. 3-MP and 4-MP concentrations were determined as 7 μg/L after 400 days of operation, and 6 μg/L after 300 days of operation, respectively.

Results showed that 2-NP concentration in the reactor was determined as 18.6 μg/L at the beginning of the operation, and maximum 4-NP concentration was determined as 38.4 μg/L. 2-NP and 4-NP concentrations both decreased below 5 μg/L after 300 days of operation. The variation of 2,4-DNP concentration was in the same trend with 2-NP and 4-NP concentrations. 2,4-DNP concentration decreased below 3 μg/L after 300 days of operation, and was determined in the range of 0.7-3 μg/L until the end of the study.

2,4-DCP concentration decreased from approximately 9 μg/L below 2 μg/L after 400 days of operation. It can be concluded that the decrease in 2,4-DCP concentrations may be explained by 2,4-DCP reduction to 4-CP. At the beginning of the landfilling operation, 2,6-DCP concentrations were determined as 17 μg/L. In 200 days of operation, no considerable change was observed in 2,6-DCP concentrations in the reactors. In methanogenic phase, 2,6-DCP concentration began to decrease and was determined below 2 μg/L after 400 days of operation. These results are consistent with Häggblom and Young [25] who concluded that 2,6-DCP reduction to 2-CP and 2-CP reduction to phenol occurred under anaerobic conditions. In our case, phenol and 2-CP concentrations increased in this phase because of 2,6-DCP degradation.

The behaviour of 2,4,5-TCP and 2,4,6-TCP contaminants determined in leachate samples showed a similar trend as other phenolic compounds. 2,4,5-TCP concentrations in the reactor reached their maximum values of 20.4 μg/L after 100 days of operation ,and decreased below 2 μg/L at the end of the study. 2,4,6-TCP concentration of leachate after 100 days of operation was determined as 321 μg/L, and in the range of 5-10 μg/L after 300 days of operation. The change in 2,4,6-TCP concentration may be explained by 2,4,6-TCP degradation under anaerobic conditions, as similarly reported by Atuanya *et al.* [26].

2,3,4,6-TeCP concentrations in leachate samples was determined at low levels compared to other phenolic compounds. At the beginning of the landfilling operation, 2,3,4,6-TeCP concentration was found to be 6.5 μg/L. Since phenolic compounds are organic contaminants, the concentrations of these organic contaminants may be expected to reduce as the leachate changes from acidogenic to methanogenic phase. This expected decreasing trend was obvious in the 2,3,4,6-TeCP concentrations. Results showed that 2,3,4,6-TeCP concentrations decreased below 1 μg/L at the end of the study. In several studies [27–29], reductive dechlorination of chlorophenols has been observed under anaerobic conditions.

In this study, PCP concentrations of leachate samples increased to maximum value of 144 μg/L after 200 days of operation. After reaching to maximum value, because of methanogenic phase, PCP concentrations began to decrease rapidly, and the concentration on day 300 was determined as 60 μg/L. The final concentrations determined in the reactor was found to be about 24 μg/L at the end of the study.

First-order kinetic model was conducted as a conceptual approach for the determination of degradation rate of the the toxic organic contaminants of leachate such as phenolic compounds. Assuming waste degradation occurs with respect to first order reaction rate, waste degradation rate coefficients of the

anaerobic reactor were calculated in respect to contaminant (phenolic compounds) removals.

First-order kinetic model equation can be expressed as follows;

$$\frac{C}{C_0} = \exp(-k \times t) \tag{1}$$

where, C is the contaminant concentration at time t, C_0 is the contaminant concentration at time t=0, k is the first-order kinetic coefficient, and t is time.

First-order kinetic model results of phenolic compounds concentrations of leachate collected from the anaerobic reactor after reaching the maximum values are given in figs. 2–5. First order degradation rates of the phenolic compounds of leachate samples collected from landfill reactor operated with leachate recirculation were calculated and the results were given in table 1.

Table 1: First order degradation rates for phenolic compounds of leachate in anerobic reactor.

Phenolic Compound	Parameter			
	k, day–1	SSE	R–square	RMSE
Phenol	0.0056	3633	0.9159	21.31
2-CP	0.0083	2375	0.9117	51.38
2-MP	0.0047	4.188	0.8781	0.647
3-MP	0.0033	16.27	0.8679	1.344
4-MP	0.0078	17.06	0.9459	1.460
2-NP	0.0059	11.11	0.9635	1.111
4-NP	0.0120	20.18	0.9828	1.497
2,4-DNP	0.0059	10.39	0.9378	1.019
2,4-DCP	0.0039	6.501	0.8521	0.849
2,6-DCP	0.0051	37.98	0.9002	2.054
2,4,5-TCP	0.0062	20.71	0.9468	1.517
2,4,6-TCP	0.0102	4125	0.9607	20.31
2,3,4,6-TCP	0.0077	10.28	0.9203	1.014
PCP	0.0096	1733	0.9170	14.72

Higher degradation rate constants (k) were calculated for 4-NP, 2,4,6-TCP and PCP that were determined as 0.0120, 0.0102 and 0.0096 day^{-1}, respectively. Lower degradation rate constants were calculated for 3-MP and 2,4-DCP that were determined as 0.0033 and 0.0039 day^{-1}, respectively. No significant differences were obtained for degradation rate constants of the rest of the phenolic compounds. First-order kinetic model fits the anaerobic degradation of

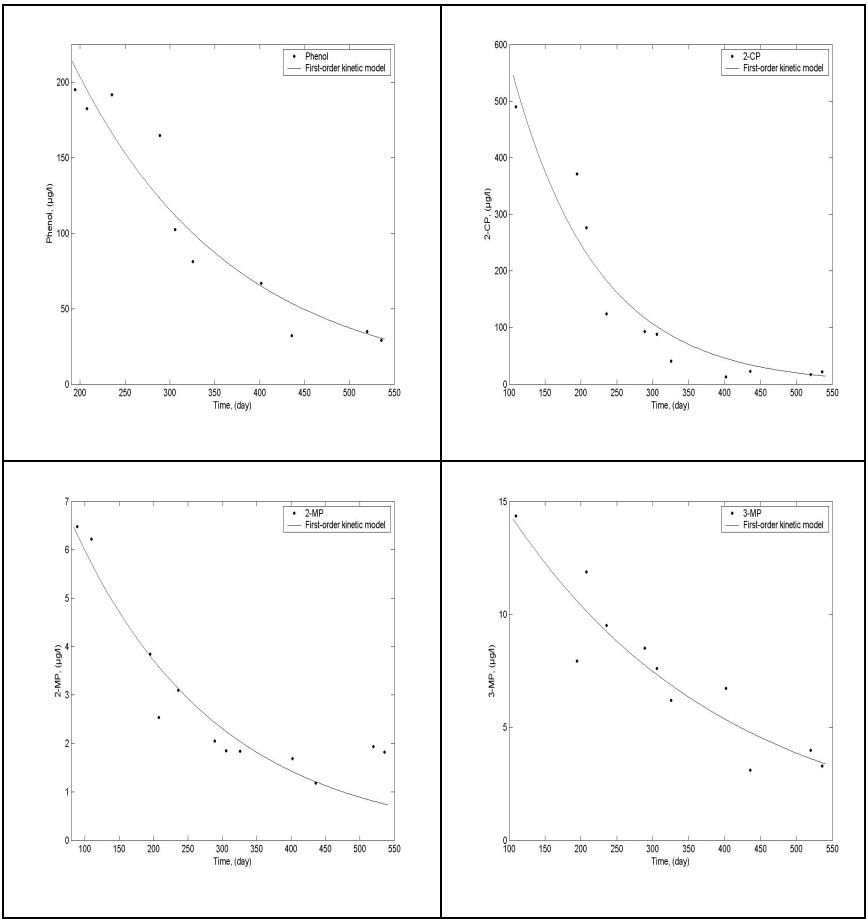

Figure 2: Kinetics of Phenol, 2-CP, 2-MP and 3-MP variations in the anaerobic reactor.

all of the phenolic compounds in leachate samples with high R^2 values. Average degradation rate of the phenolic compounds was determined to be 0.0068 day^{-1}.

A well-fitting regression model results in predicted values close to the observed data values. R-squared has the useful property that its scale is intuitive: it ranges from zero to one, with zero indicating that the proposed model does not improve prediction over the mean model and one indicating perfect prediction. Improvement in the regression model results in proportional increases in R-squared.

The RMSE is the square root of the variance of the residuals. It indicates the absolute fit of the model to the data–how close the observed data points are to the model's predicted values and SSE measures how far the data are from the model's predicted values.Whereas R-squared is a relative measure of fit, RMSE is an absolute measure of fit. As the square root of a variance, RMSE can be

interpreted as the standard deviation of the unexplained variance, and has the useful property of being in the same units as the response variable. Lower values of RMSE and SSE indicate better fit. RMSE is a good measure of how accurately the model predicts the response, and is the most important criterion for fit if the main purpose of the model is prediction.

Highest RMSE and SSE values were obtained for degradation of phenolic compounds (phenol, 2-Chlorophenol (2-CP), 2,4,6-Trichlorophenol (2,4,6-TCP) and Pentachlorophenol (PCP)). Lower RMSE and SSE values obtained for degradation of phenolic compounds (2-Metilphenol (2-MP), 3-Metilphenol (3-MP), 4-Metilphenol (4-MP), 2-Nitrophenol (2-NP), 4-Nitrophenol (4-NP), 2,4-Dinitrophenol (2,4-DNP), 2,4-Dichloropenol (2,4-DCP), 2,6-Dichloropenol (2,6-DCP), 2,4,5-Trichlorophenol (2,4,5-TCP), 2,3,4,6-Tetrachlorophenol (2,3,4,6-TeCP)) indicate better fit to the first-order kinetic model. All of the R^2 values were determined to be high, close to 1 (R^2 >0.85) indicating good prediction.

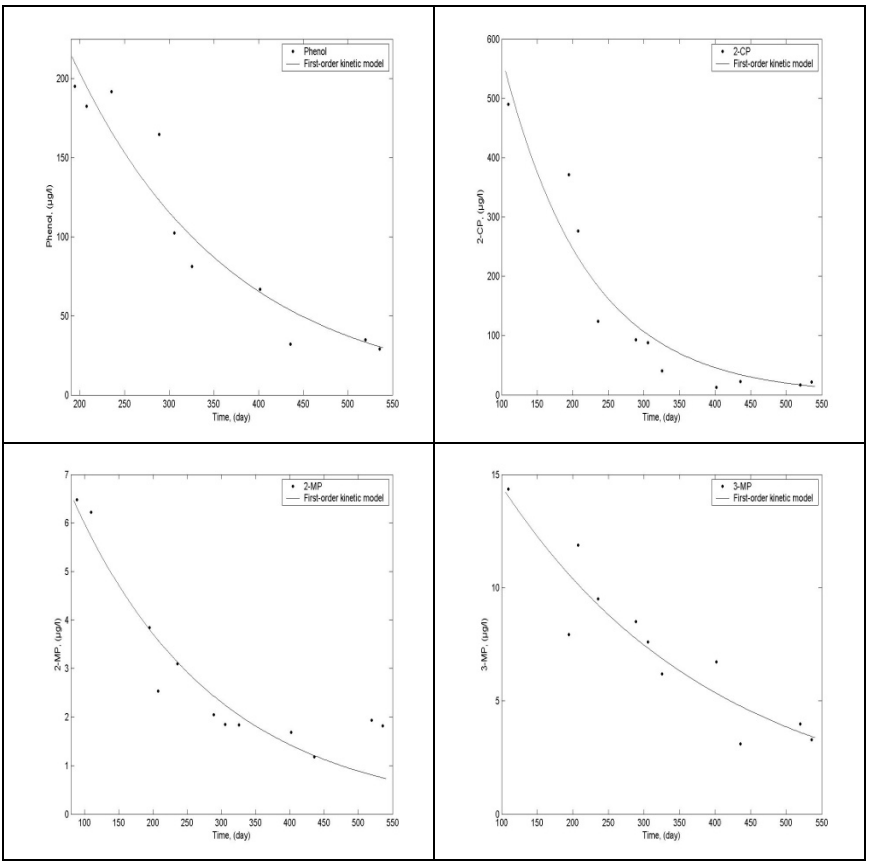

Figure 3: Kinetics of 4-MP, 2-NP, 4-NP and 2,4-DNP variations in the anaerobic reactor.

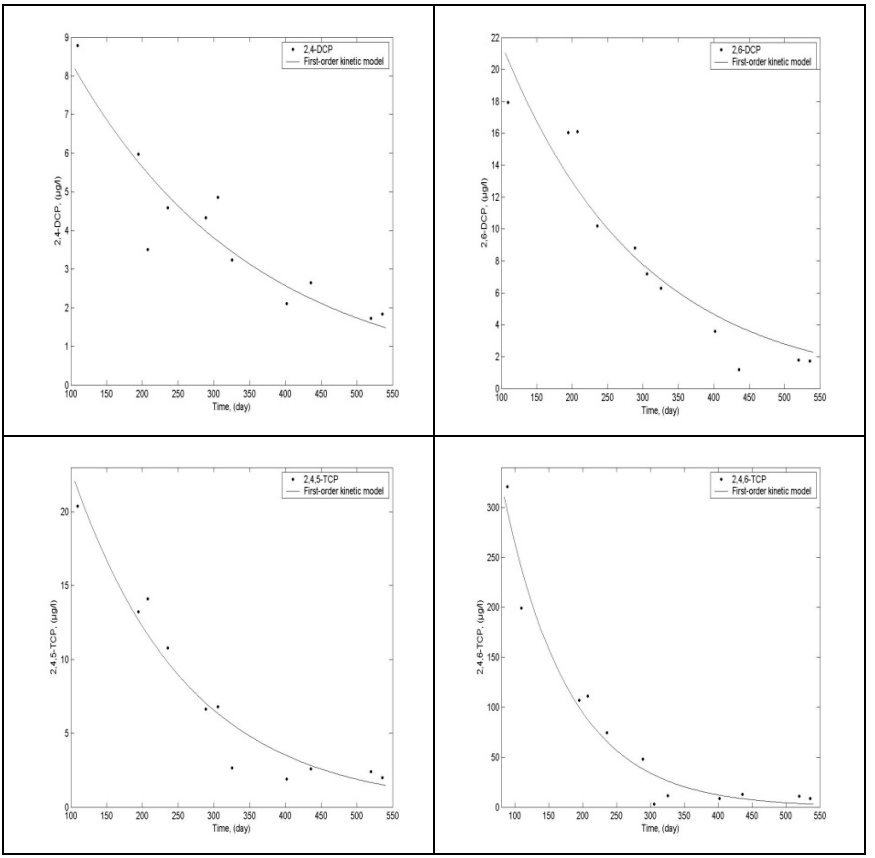

Figure 4: Kinetics of 2,4-DCP, 2,6-DCP, 2,4,5-TCP and 2,4,6-TCP variations in the anaerobic reactor.

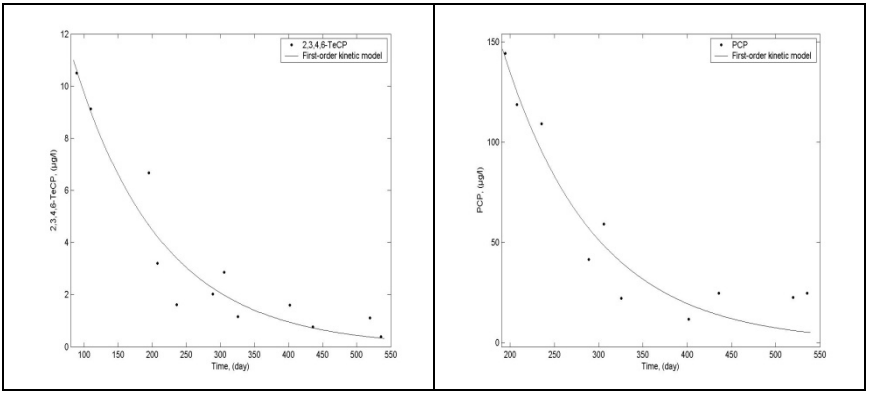

Figure 5: Kinetics of 2,3,4,6-TeCP, and PCP variations in the anaerobic reactor.

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