CHAPTER IV

RESULTS

4.1. Soil Properties

Soil sample was collected from cassava agricultural area in Nakhonratchasima province, Thailand at the depth of 2-10cm. The soil samples were sieved through 2 mm mesh. Then, they were analyzed for their physical and chemical properties at Department of Soil Science, Faculty of Agriculture, Kasetsart University and Soil and Water Group, Agricultural Chemistry Division.

The soil properties are provided in Table 4.1. Soil is classified as silty clay soil with 13.6% sand, 40.4% silt and 46.0% clay. pH value of soil was 7.03. Percentage of organic matter was 3.93. Moisture content was 15.57%. Cation Exchange Capacity was 26.00 $cmol.kg^{-1}$. Surface area was 30.12 $m^2.g^{-1}$. Electrical capacity was 420 $\mu S.cm^{-1}$. Amount of available Phosphorus, Potassium, Calcium, Magnesium, Iron, Manganese and Zinc were 169, 331, 8853, 321, 3.33, 5.10 and 0.63 ppm, respectively.

Table 4.1 Properties of soil samples

Properties	Soil sample
Soil texture	Silty Clay
% sand	13.60
% silt	40.40
% clay	46.00

pH (1:1) in water	7.03
Organic matter (%)	3.93
Moisture (%)	15.75
Cation Exchange Capacity; CEC (cmol kg^{-1})	26.00
Surface area ($m^2 g^{-1}$)	30.12
Electrical capacity ($\mu S\ cm^{-1}$)	420.00
Available phosphorus (ppm)	169.00
Potassium; K (ppm)	331.00
Calcium; Ca (ppm)	8853.00
Magnesium; Mg (ppm)	321.00
Iron; Fe (ppm)	3.33
Manganese; Mn (ppm)	5.10
Zinc; Zn (ppm)	0.63

4.2 Diuron and Diuron80 Solubility

In the initial of experiment, screening of solvent is necessary for selection of organic solvent and surfactant to use in soil washing experiment of soil contaminated with diuron and commercial diuron (diuron80). The method is shown in 3.5 and the results are shown in Table 4.2

From Table 4.2, diuron has good solubility (>80%) in methanol and *n*-butanol, moderate solubility in ethanol, *sec*-butanol, toluene, benzene and acetone, low solubility in Triton X-100, Tergitol NP10, Tween80, Brij35 and SDS. For commercial grade diuron 80 has good solubility in methanol, ethanol and *n*-butanol, moderate solubility in *sec*-butanol, toluene, benzene and acetone, low solubility in Triton X-

100, Tergitol NP10, Tween80, Brij35 and SDS. Both diuron and diuron 80 were not soluble in water, *n*-octanol and hexane, therefore hexane and *n*-octanol were not used for soil washing experiment, water and calcium chloride solution were used for control experiment.

Table 4.2 Solubility of diuron and diuron80 in various organic solvents and chemical surfactants at room temperature (25°C)

Solvent	Solubility					
	Diuron			Diuron80		
		$mg.ml^{-1}$	% w/w		$mg.ml^{-1}$	% w/w
water	o	0.05±0.00	5±0	o	0.07±0.01	7±1
Methanol	***	0.95±0.03	95±3	***	0.96±0.03	96±3
Ethanol	**	0.77±0.05	77±5	***	0.96±0.03	96±3
n-Butanol	***	1.01±0.03	100±3	***	0.95±0.02	95±2
sec-Butanol	**	0.77±0.03	77±3	**	0.78±0.02	78±2
n-Octanol	o	0.00±0.00	0±0	o	0.00±0.00	0±0
Toluene	**	0.77±0.02	77±2	**	0.73±0.03	73±3
Benzene	**	0.61±0.03	61±3	**	0.69±0.03	69±3
Acetone	**	0.75±0.04	75±4	**	0.76±0.05	76±5
n-Hexane	o	0.00±0.00	0±0	o	0.00±0.00	0±0
Triton X-100	*	0.29±0.02	29±2	*	0.38±0.01	38±1
Tergitol NP10	*	0.18±0.00	18±0	*	0.34±0.01	34±1
Tween80	*	0.25±0.01	25±1	*	0.34±0.01	34±1
Brij35	*	0.19±0.00	19±0	*	0.20±0.01	20±1
SDS	*	0.19±0.01	19±1	*	0.29±0.01	29±1

*** = good solubility, no particulates (>80%)

** = moderate solubility and some particulates (50-80%)

* = low solubility, many particulates (10-50%)

o = not soluble (<10%)

4.3 Contaminant Adsorption Isotherms

In general, the adsorption of hydrocarbon contaminants from aqueous solution occurs by hydrophobic bonding between the contaminant and the surface. This kind of adsorption has been called "solvent-disliking" adsorption and is primarily driven by the entropy decrease that occurs when the water molecules around the solubilized contaminant are released when the contaminant adsorbs (Weber, 1970). Since sorption of organic pollutant, i.e. diuron, to soil is one of the most influential factors on its transport and fate in natural system. Therefore, the sorptive behaviors, i.e. the sorption isotherm, of both diuron and diuron80, were essentially carried out in order to describe the fate of diuron contaminated in soil. In order to know the behavior of adsorption with increasing concentration of diuron, the amounts of the herbicide adsorbed were plotted against the equilibrium concentrations of the herbicide. The method is shown in Method 3.5 and the experiment data for adsorption isotherm studies of both diuron and diuron80 are shown in Appendix D. According to Figure 4.1 and 4.2, the slope of the sorption isotherm of diuron and diuron80 in soil may be classified as a linear type of the Giles isotherm classification, which suggests that this soil has an average affinity by the herbicide diuron and that there is moderate competition from the solvent for sorption sites. When the amount of contaminant adsorbed per unit mass of carbon was plotted on a log-log scale with the contaminant in the bulk phase (Figure 4.3, 4.4), the intercept of linear curve (at the equilibrium concentration equal to 1) is equal to 1.275 mg.kg^{-1} soil (K_f = 16.69 mg.kg^{-1} soil) and 1.223 mg.kg^{-1} soil (K_f = 18.85 mg.kg^{-1} soil) for diuron isotherm and diuron80 isotherm, respectively. The slopes (Freundlich exponent, n) of the diuron and diuron80 isotherms are equal to 1.033 (r^2 = 1) and 0.997 (r^2 = 1), respectively.

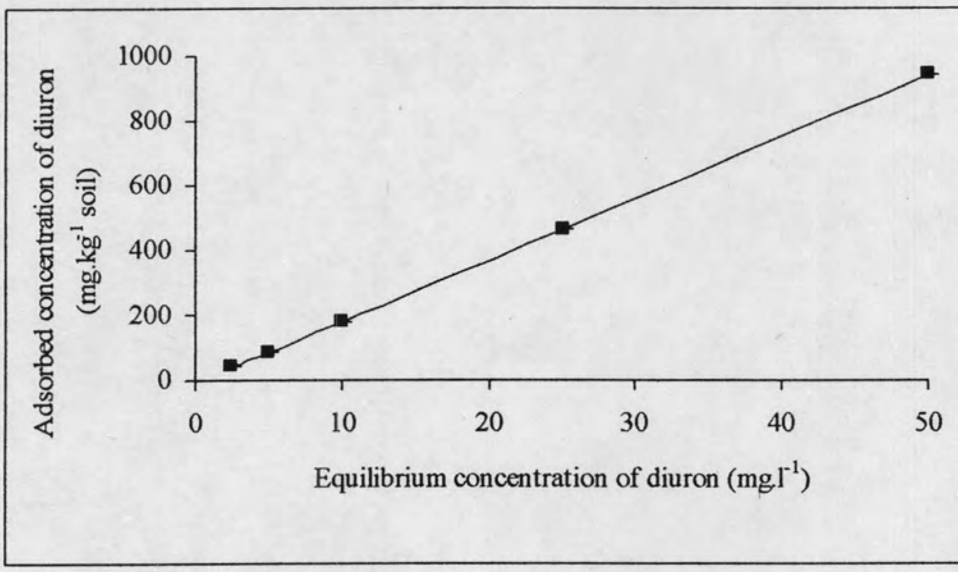


Figure 4.1 Adsorption isotherm of diuron on soil

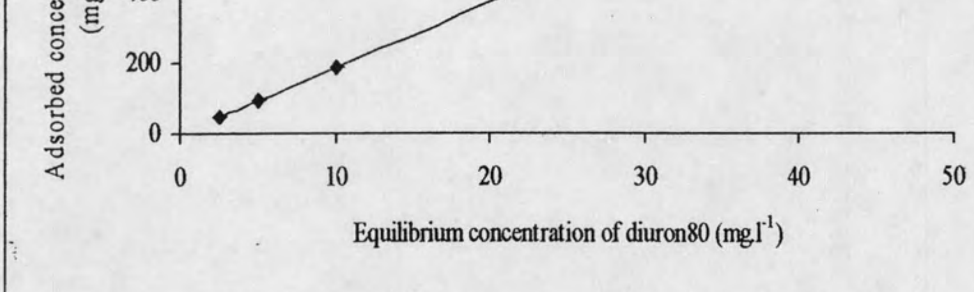


Figure 4.2 Adsorption isotherm of diuron80 on soil

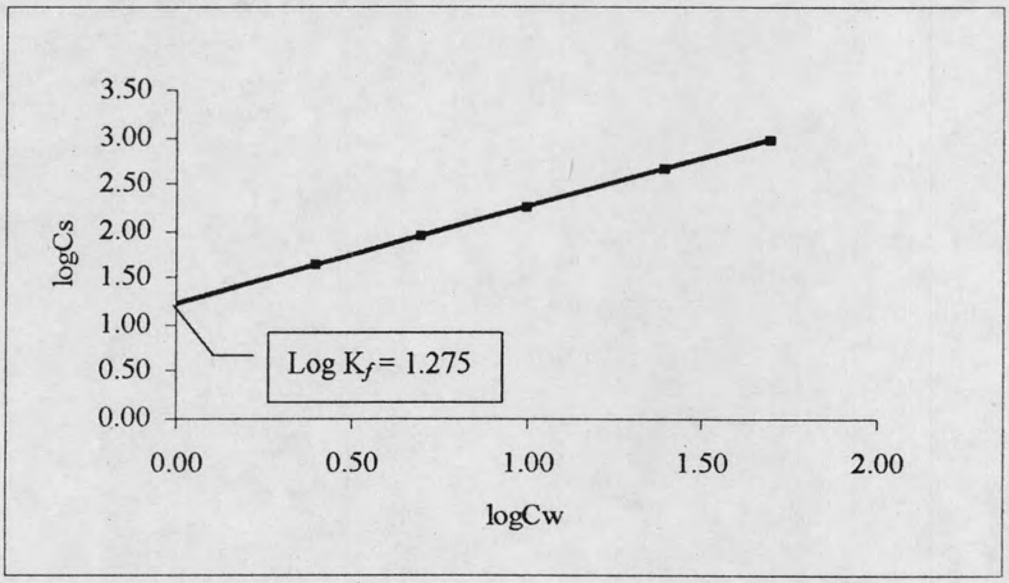


Figure 4.3 Freundlich adsorption isotherm of diuron on soil, C_s is milligrams of diuron sorbed per kilogram of soil, C_w is the equilibrium solution concentration (mg dm^{-3})

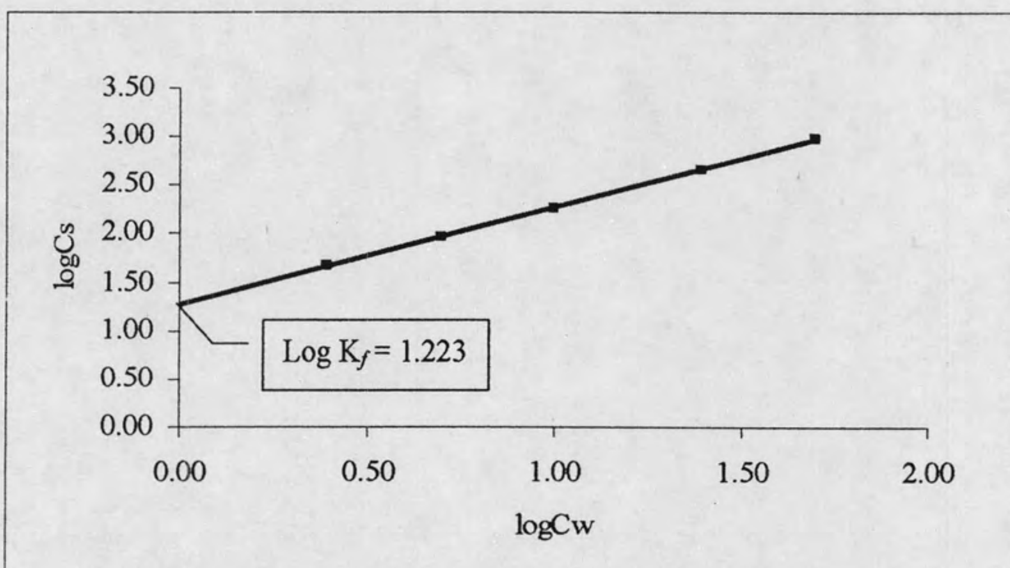


Figure 4.4 Freundlich adsorption isotherm of diuron80 on soil, C_s is milligrams of diuron sorbed per kilogram of soil, C_w is the equilibrium solution concentration (mg dm^{-3})

4.4 Soil Washing Experiment

4.4.1 Pretreatment of diuron contaminated soil using 0.01 M $CaCl_2$

From the Method 3.6.1, the column volume of soil column is 100 ml. The result of pretreatment diuron contaminated soil column using 0.01 M $CaCl_2$ was shown in Figure 4.5. The graph is plotted between percentage of diuron concentration leached from soil column and sample fraction (one fraction is 100 ml). The result shows that unbound and loosely bound diuron was leached by calcium chloride solution within the first five fractions. After 5th fraction, diuron was no longer significant eluted out from the column. Therefore, throughout the soil washing experiment, the pretreatment was carried out with 5 column volume (500 ml) of calcium chloride solution for soil column condition and 50 ml of calcium chloride solution for shaking condition.

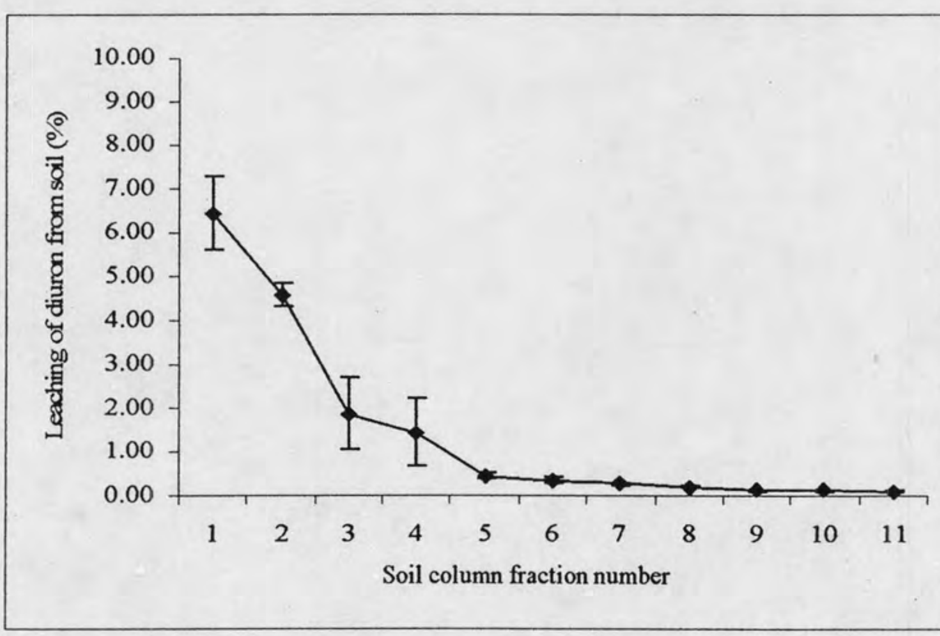


Figure 4.5 Pretreatment of soil column using 0.01M $CaCl_2$

4.4.2 Determination of leaching conditions of diuron-contaminated soil using soil column

The method and the experiment data of the soil washing study are given in Method 3.6.2.1 and Appendix D, respectively. The leaching conditions of contaminated soil were investigated in soil column. The parameters involving the leaching conditions were as followed: a) type of diuron, i.e. a relatively pure diuron and diuron80 (a commercial grade) in which pesticide/herbicide adjuvant are included; b) aging period of diuron in soil; c) treatment conditions, i.e. soil column and shaking-flask; d) types and concentrations of organic solvents and e) types and concentrations of surfactants used to facilitate the leaching.

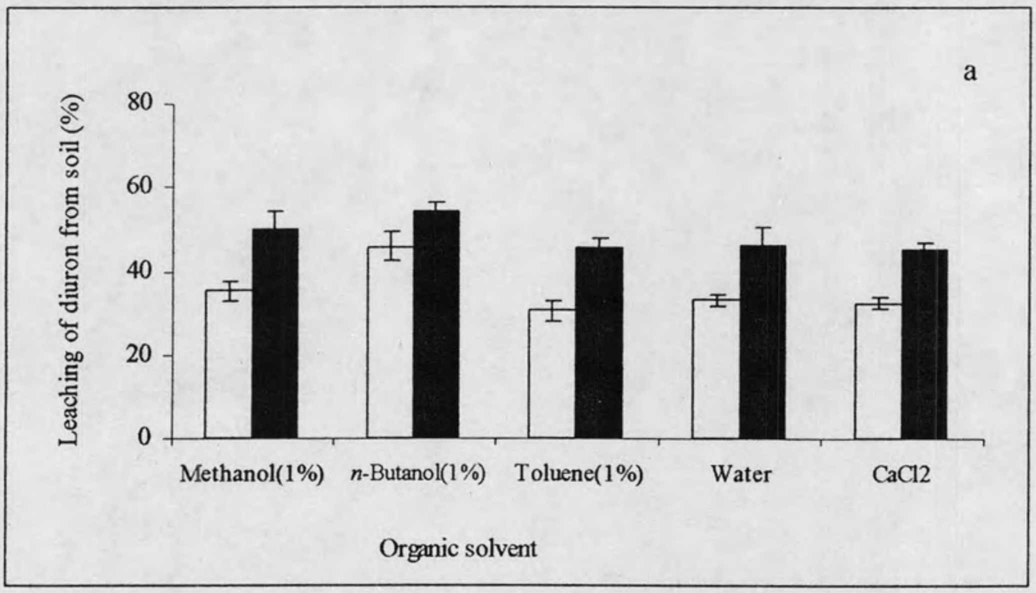
The leaching efficiency of diuron from soil using organic solvent was studied in static condition using soil column (Method 3.6.2.1) and monitored by HPLC analysis. Leaching of diuron by either organic solvent or chemical surfactant was carried out after 5 column volume of pretreatment with calcium chloride solution. Leaching performances, raw data and calculation were shown in Appendix D. The investigation was first carried out with 1-week diuron-aged soil (Figure 4.6 and Table 4.3). Three common organic solvents used for soil washing, i.e. methanol, *n*-butanol and toluene, were applied onto soil column at 1% (v/v). Leaching efficiencies of diuron from soil using *n*-butanol (45.83±3.41% w/w) was higher than methanol (35.38±2.38% w/w) and toluene (30.36±2.56% w/w) (Figure 4.6a). Leaching efficiency of organic solvent tested toward commercial-grade diuron80 from soil was higher, i.e. *n*-butanol (54.31±2.24% w/w), methanol (49.97±4.20% w/w), and toluene (45.44±2.54% w/w) (Figure 4.6a).

When effect of chemical surfactants (2CMC of TritonX-100 and SDS) on leaching of diuron was determined, the leaching efficiencies were 32.80±1.69% w/w and 36.83±0.55% w/w for diuron and 39.62±1.52% w/w and 44.02±3.54% w/w for diuron80, respectively (Figure 4.6b), the results show leaching efficiency using SDS was higher than Triton X-100. For control experiment (water and calcium chloride solution), the leaching efficiencies were 33.03±1.55% w/w and 32.48±1.51% w/w for diuron and 46.31±3.91% w/w and 45.32±1.33% w/w for diuron80, respectively. Interestingly, leaching efficiency of organic solvent and surfactant was nearly control (water and calcium chloride solution), and leaching efficiency tested toward commercial-grade diuron80 from soil was higher than diuron about 10-15% w/w, approximately, suggesting that it was comparatively loosely bound to soil.

These results indicated that organic solvents and chemical surfactants can be used with fair leaching efficiency for soil washing of short-term soil contamination of diuron.

Table 4.3 Leaching of 1-week diuron- and diuron80-aged soil packed in soil column using organic solvent and surfactant.

Organic solvent and surfactant	Leaching of diuron from soil	
	Diuron (% w/w)	Diuron80 (% w/w)
Methanol (1% v/v)	35.38±2.38	49.97±4.20
n-Butanol (1% v/v)	45.83±3.41	54.31±2.24
Toluene (1% v/v)	30.36±2.56	45.44±2.54
Triton X-100 (2 CMC)	32.80±1.69	39.62±1.52
SDS (2 CMC)	36.83±0.55	44.02±3.54
Water	33.03±1.55	46.31±3.91
0.01 M $CaCl_2$	32.48±1.51	45.32±1.33



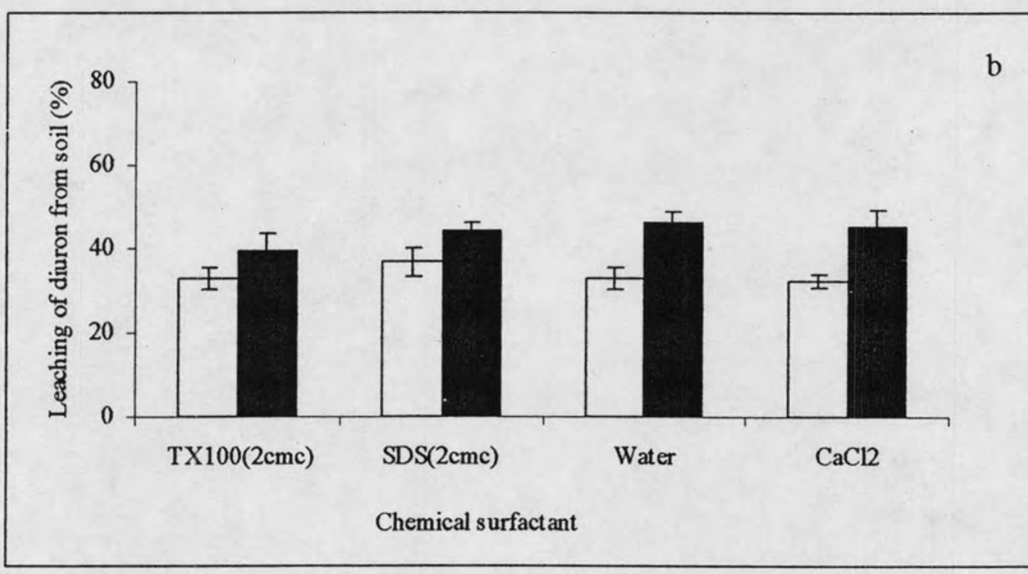


Figure 4.6 Leaching of 1-week diuron-aged soil (□) and 1-week diuron80-aged soil (■) packed in soil column using a) organic solvents (Methanol, *n*-Butanol and Toluene) and b) chemical surfactants (TritonX-100; TX100 and Sodium dodecyl sulphate; SDS). The concentration of organic solvent (v/v) and surfactant is shown in bracket. (These results are the mean of 6 individual experiments)

The investigation of effect of soil-aging on leaching was carried out in more details with 1-month diuron/diuron80-aged soil where the stronger sorption of diuron onto soil was expected to be higher. Effect of various types and concentrations (1%, 5% and 10% v/v) of organic solvents as well as chemical surfactants (1, 2, 8 and 20 CMC) on leaching efficiency of diuron/diuron80 from soil were determined. The results show that comparatively similar patterns of organic solvent-aided leaching efficiency were obtained for diuron and diuron80 (Figure 4.7 and Table 4.4). The determination of leaching efficiency using various types and concentrations of chemical surfactants was then examined (Figure 4.8 and Table 4.5).

Leaching of diuron from soil using the soil column treatment by 1% (v/v) concentration of short chain alcohols, results show *n*-butanol exhibited the highest leaching efficiency (40.49±3.32% w/w), followed by *sec*-butanol (34.69±1.48% w/w), methanol (32.13±1.81% w/w), and ethanol (27.08±1.78% w/w), respectively, while the leaching efficiency were increased to 45.31±1.79% w/w, 39.32±1.94% w/w, 32.75±2.61% w/w and 30.68±1.24% w/w, respectively when the concentration of organic solvent was increased to 5% (v/v). When the concentration was increased to 10% (v/v), leaching efficiency was increased to 50.99±2.32% w/w, 42.25±2.35% w/w, 41.92±0.88% w/w and 33.84±0.91% w/w, respectively.

The same trend was observed in leaching of diuron80 from soil using the soil column treatment by 1% (v/v) concentration of short chain alcohols, results show *n*-butanol (47.56±4.09% w/w) exhibited the highest leaching efficiency, followed by *sec*-butanol (37.82±2.31% w/w), methanol (36.51±4.22% w/w) and ethanol (29.35±3.96% w/w), respectively, while the leaching efficiency were increased to 53.94±2.68% w/w, 45.26±1.60% w/w, 37.87±4.76% w/w and 35.58±4.17% w/w, respectively when the concentration of organic solvent was increased to 5% (v/v).

When the concentration was increased to 10% (v/v), leaching efficiency was increased to 72.95±1.70% w/w, 51.27±2.27% w/w, 52.49±3.25% w/w and 41.88±4.29% w/w, respectively. Interestingly, leaching of diuron and diuron80 from soil by *sec*-butanol resulted in less leaching efficiency than its isomer (*n*-butanol).

Leaching of diuron using long-chain organic solvents (1% v/v) was also examined. According to previous result on diuron and diuron80 solubility shown in Table 4.2, diuron could be solubilized in toluene (0.77±0.02 $mg.ml^{-1}$), benzene (0.61±0.03 $mg.ml^{-1}$) and acetone (0.75±0.04 $mg.ml^{-1}$), and for diuron80 could be solubilized in toluene (0.73±0.03 $mg.ml^{-1}$), benzene (0.69±0.03 $mg.ml^{-1}$) and acetone (0.76±0.05 $mg.ml^{-1}$), respectively. However, it was not solubilized in hexane and *n*-octanol. Therefore, leaching of diuron and diuron80 using only toluene, benzene and acetone were further studied.

The leaching efficiencies of diuron using these organic solvents (toluene, benzene and acetone) at 1% (v/v) were comparatively similar, which are approximately 29.95±0.89% w/w, 31.12±0.29% w/w and 29.35±2.41% w/w, respectively. The leaching efficiencies of diuron80 using these organic solvents which are approximately 36.03±2.27% w/w, 33.84±2.10% w/w and 31.40±1.75% w/w, respectively. The investigation using toluene, benzene and acetone at high concentration was limited because they have high viscosity and difficult to pass through soil column. Moreover, on the contrary to short-chain alcohols, at higher concentration they become more toxic (Reichardt, 1998).

From results desorbed above, it was shown that *n*-butanol at the concentration 10% (v/v) exhibited the highest leaching efficiency (50.99±2.32% w/w and 72.95±1.70% w/w for diuron and diuron80, respectively) when compared to other organic solvents that were used in experiment. Moreover, leaching efficiency was increased with increasing of concentration of organic solvent.

Leaching efficiencies with chemical surfactants were examined in the range of concentration 1, 2, 8 and 20 CMC (Table 4.5 ad Figure 4.8). However, higher concentration of SDS than 2 CMC was avoided because it dispersed soil particles obstructing liquid flow in the column. Therefore, SDS was used at low concentration (1 and 2 CMC).

Leaching of diuron and diuron80 from soil using the soil column treatment by nonionic surfactants, i.e. Triton X-100, Tergitol NP10, Tween80 and Brij35, was examined. At low concentration (1, 2 and 8 CMC), increasing of surfactant concentrations did not have much effect in enhancing the leaching of diuron. Leaching efficiency varied from 25.56±1.56 to 32.93±2.10% w/w for diuron, and 28.01±.1.73 to 36.65±2.39% w/w for diuron80, respectively. However, leaching efficiency was increased when the concentration of surfactant was increased to 20 CMC. Leaching improvement was found to be in the range of 3-10% w/w, approximately. The results varied from 30.59±1.70 to 39.68±2.73% w/w for diuron, and 36.25±2.96 to 45.07±1.19% w/w for diuron80, respectively.

For leaching efficiency using 1 CMC and 2 CMC anionic surfactant, SDS, the results show increasing of SDS concentrations did not have much effect in enhancing the leaching of diuron and diuron80, resulted in 32.77±0.14% w/w and 30.22±1.48% w/w for diuron, and 40.22±1.56% w/w and 41.85±4.01% w/w for diuron80, respectively. However, leaching efficiency of diuron80 using SDS is higher than nonionic surfactant at the same concentration in the range of 5-10% w/w, approximately. Results of control experiment (using water or calcium chloride solution.) were 29.35±2.41%% w/w and 27.12±2.37% w/w for diuron and 28.87±1.38% w/w and 30.38±0.68% w/w, respectively.

From results of leaching efficiency by surfactant, similar results were observed for each surfactant. The results show insignificant different of leaching efficiency using various surfactants (Triton X-100, Tergitol NP10, Tween80, Brij35 and SDS). However, TritonX-100, a nonionic surfactant, has highest leaching efficiency at high concentration (20 CMC) when compared to other surfactants that were used in experiment, which are approximately 39.68±2.73% w/w and 45.07±1.19% w/w for diuron and diuron80, respectively. Moreover Triton X-100 was previously reported to be the most suitable surfactant due to its short polyoxyethylene hydrophilic chain resulting in its high capacity for enhancing solubility of xenobiotic compounds. The longer hydrophilic chain of surfactant was found to hinder the interaction between the micelles and soil surface (Edwards et al., 1991).

Interestingly, leaching efficiency of 1-month diuron- and diuron80-aged soil (Table 4.4 and 4.5) resulted in less leaching efficiency when compared to that of 1-week diuron- and diuron80-aged soil (Table 4.3). These results suggest that long-term contamination of diuron may cause a stronger sorption onto soil. Aging of pesticide/herbicide residue leads to increased sorption and reduced availability for leaching. As for the static condition, organic solvents-aided soil washing is probably a more suitable treatment for the relatively long-term soil contamination of diuron/diuron80 than that with chemical surfactants, with the fact that *n*-butanol-facilitated soil washing yielded the highest leaching efficiency. Nonetheless, leaching efficiency with diuron80 was higher than that with diuron indicating that diuron80 has higher water solubility.

Table 4.4 Leaching of 1-month diuron- and diuron80-aged soil packed in soil column using organic solvent.

Organic solvent	Leaching of diuron from soil	
	Diuron (% w/w)	Diuron80 (% w/w)
Methanol (1% v/v)	32.13±1.81	36.51±4.22
Methanol (5% v/v)	32.75 ±2.61	37.87±4.76
Methanol (10% v/v)	41.92±0.88	52.49±3.25
Ethanol (1% v/v)	27.08±1.78	29.35±3.96
Ethanol (5% v/v)	30.68±1.24	35.58±4.17
Ethanol (10% v/v)	33.84±0.91	41.88±4.29
n-Butanol (1% v/v)	40.49±3.32	47.56±4.09
n-Butanol (5% v/v)	45.31±1.79	53.94±2.68
n-Butanol (10% v/v)	50.99±2.32	72.95±1.70
sec-Butanol (1% v/v)	34.69±1.48	37.82±2.31
sec-Butanol (5% v/v)	39.32±1.94	45.26±1.60
sec-Butanol (10% v/v)	42.25±2.35	51.27±2.27
Toluene (1% v/v)	29.95±0.89	36.03±2.27
Benzene (1% v/v)	31.12±0.29	33.84±2.10
Acetone (1% v/v)	29.35±2.41	31.40±1.75
Water	29.35±2.41	28.87±1.38
0.01 M $CaCl_2$	27.12±2.37	30.38±0.68

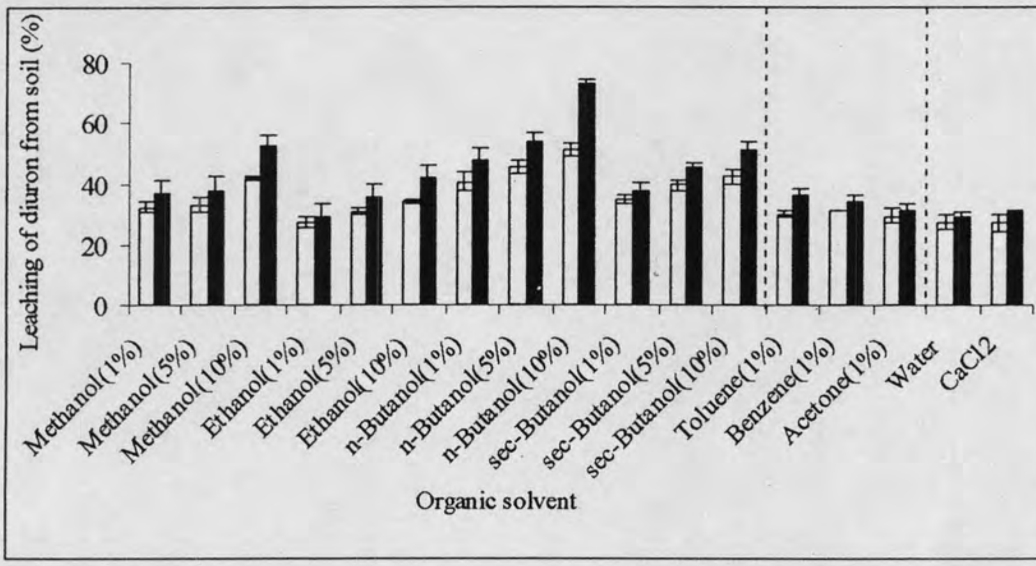


Figure 4.7 Leaching of 1-month diuron-aged soil (□) and 1-month diuron80-aged soil (■) packed in soil column using organic solvents. The concentration is shown in bracket. (These results are the mean of 6 individual experiments)

Table 4.5 Leaching of 1-month diuron- and diuron80-aged soil packed in soil column using surfactant.

Surfactant	Leaching of diuron from soil	
	Diuron (% w/w)	Diuron80 (% w/w)
Triton X-100 (1 CMC)	32.34±1.33	35.34±1.87
Triton X-100 (2 CMC)	32.29±1.85	34.67±2.00
Triton X-100 (8 CMC)	31.21±1.97	37.17±1.36
Triton X-100 (20 CMC)	39.68±2.73	45.07±1.19
Tergitol NP10 (1 CMC)	32.70±2.29	35.19±1.34
Tergitol NP10 (2 CMC)	28.41±1.76	30.76±3.52
Tergitol NP10 (8 CMC)	30.33±0.68	32.57±2.79

Tergitol NP10 (20 CMC)	30.73±0.41	41.32±0.51
Tween80 (1 CMC)	32.54±1.62	36.65±2.39
Tween80 (2 CMC)	27.66±1.62	31.87±0.86
Tween80 (8 CMC)	31.03±0.14	35.41±2.78
Tween80 (20 CMC)	35.77±1.37	42.46±0.98
Brij35 (1 CMC)	32.93±2.10	31.13±2.52
Brij35 (2 CMC)	25.56±1.56	28.01±1.73
Brij35 (8 CMC)	29.00±0.62	30.47±1.33
Brij35 (20 CMC)	30.59±1.70	36.25±2.96
SDS (1 CMC)	32.77±0.14	40.22±1.56
SDS (2 CMC)	30.20±1.48	41.85±4.01
Water	27.12±2.37	28.87±1.38
0.01 M $CaCl_2$	27.05±2.76	30.38±0.68

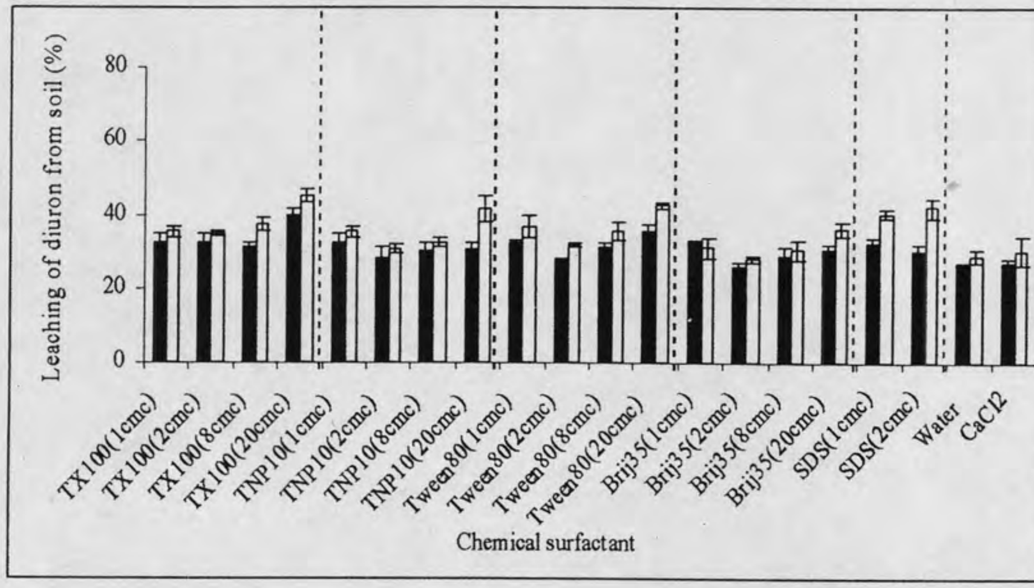


Figure 4.8 Leaching of 1-month diuron-aged soil (□) and 1-month diuron80-aged soil (■) packed in soil column using chemical surfactants. The concentration is shown in bracket. (These results are the mean of 6 individual experiments)

4.4.3 Determination of leaching conditions of diuron-contaminated soil using mixing condition (shaking-flask)

The leaching conditions of diuron/diuron80-contaminated soil were investigated using a mixing condition, as it could be useful as laboratory-scale informative data for an *ex situ* soil washing treatment.

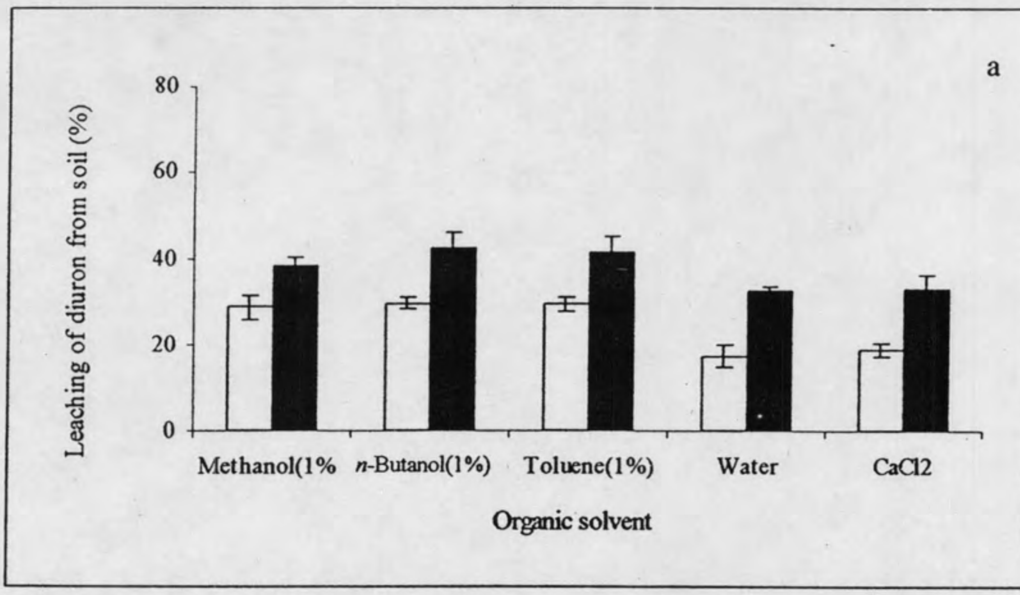
The investigation of shaking-condition leaching was done with the same contaminated soil: diuron ratio (10 g : 1 mg) as it was used in the static condition. The results in Figure 4.9-4.11 were total leaching of diuron from soil (% w/w) by 50 ml of organic solvent or chemical surfactant after pretreated soil with calcium chloride solution. With the similar approaches done with the soil column experiments, while the leaching of diuron and diuron80 from 1-week diuron-aged soil with shaking conditions was investigated. When three common organic solvents (1% v/v of methanol, *n*-butanol and toluene) or chemical surfactants (2 CMC of TritonX-100 and SDS) was applied (Figure 4.9 and Table 4.6), leaching efficiency of diuron were approximate 28.52±2.67% w/w, 29.48±1.36% w/w, 29.31±1.78% w/w, 26.20±1.67% w/w and 30.99±1.45% w/w, respectively, leaching efficiency of diuron80 were approximated 38.11±2.16%% w/w, 42.46±3.32% w/w, 41.35±3.50% w/w, 41.07±2.57% w/w and 44.85±4.07% w/w, respectively. These results indicated that organic solvents and chemical surfactants can be used with fair leaching efficiency for soil washing of short-term soil contamination of diuron. However, leaching efficiency using these organic solvent or surfactant was higher than control experiment (water and calcium chloride solution), which the leaching efficiencies were 17.14±2.55 and 18.73±1.45 for diuron and 32.65±0.78 and 33.11±2.75 for diuron80, respectively.

These results suggesting that either diuron or diuron80 was loosely bound to soil when it was mixed and incubated for a short period of time, i.e. one week. Therefore, it could be loosely washed off the soil with shaking condition. Nonetheless, leaching efficiency with diuron80 was higher than that with diuron about 10-15% w/w, approximately, indicating that diuron80 has higher water solubility.

Table 4.6 Leaching of 1-week diuron- and diuron80-aged soil under a shaking condition using organic solvent and surfactant.

Organic solvent and surfactant	Leaching of diuron from soil	
	Diuron (% w/w)	Diuron80 (% w/w)
Methanol (1% v/v)	28.52±2.67	38.11±2.16
n-Butanol (1% v/v)	29.48±1.36	42.46±3.32
Toluene (1% v/v)	29.31±1.78	41.35±3.50
Triton X-100 (2 CMC)	26.20±1.67	41.07±2.57

SDS (2 CMC)	30.99±1.45	44.85±4.07
Water	17.14±2.55	32.65±0.78
0.01 M $CaCl_2$	18.73±1.45	33.11±2.75



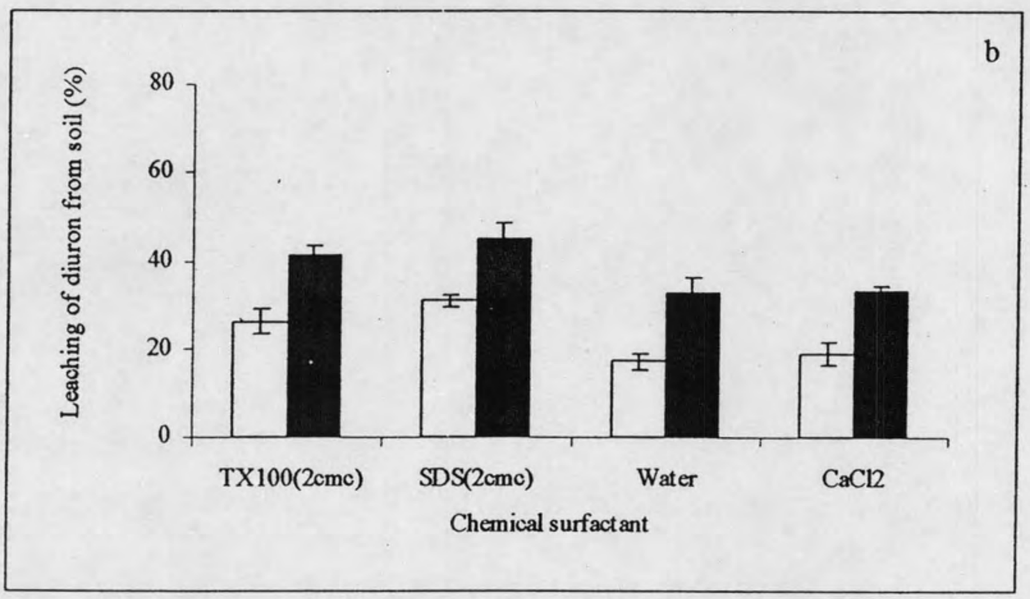


Figure 4.9 Leaching of 1-week diuron-aged soil (□) and 1-week diuron80-aged soil (■) under a shaking condition using a) organic solvents and b) chemical surfactants. The concentration is shown in bracket. (These results are the mean of 6 individual experiments)

The leaching study was then examined with 1-month diuron/diuron80-aged soil using organic solvent (Figure 4.10 and Table 4.7). It was found that in shaking conditions, types of organic solvents used showed less significant effect on leaching efficiency. When short chain organic solvents (methanol, ethanol, *n*-butanol and *sec*-butanol) were used at 1% (v/v), leaching efficiency valued from 15.76±2.33 to 27.60±1.48% w/w for diuron and 27.97±3.44 to 33.82±4.74% w/w for diuron80, respectively, whereas it was increased varied from 21.07±2.72 to 27.51±2.57% w/w for diuron and 30.94±3.15 to 40.63±3.06% w/w for diuron80, respectively, when concentration of these organic solvents was increased to 5% (v/v). Increasing of the concentration of these organic solvents, to 10% (v/v) enhanced the leaching efficiency varied from 27.80±2.12 to 37.03±0.99% w/w for diuron and 36.05±4.44 to 48.83±3.34% w/w for diuron80, respectively. The highest leaching efficiency was obtained from the treatment with 10% (v/v) *n*-butanol (37.03±0.99% w/w and 48.83±3.34% w/w for diuron and diuron80, respectively), similar to that soil column condition.

The leaching study was then examined with 1-month diuron/diuron80-aged soil using surfactant (Figure 4.11 and Table 4.8). When effect of various types and concentrations of nonionic surfactants (Triton X-100, Tergitol NP10, Tween80 and Brij35) were examined, leaching efficiency of each treatment was comparatively similar at low concentration (1, 2 and 8 CMC). Leaching efficiency varied from 16.52±1.52 to 21.01±2.00% w/w for diuron, and 25.90±.2.66 to 35.60±3.51% w/w for diuron80, respectively. When concentration was increased to 20 CMC, leaching efficiency has increase about 3-6% w/w, approximately. The results varied from 20.77±0.93 to 25.55±2.00% w/w for diuron, and 33.66±0.86 to 40.39±2.97% w/w for diuron80, respectively.

For leaching efficiency using 1 CMC and 2CMC anionic surfactant, SDS, the results show higher leaching efficiency than nonionic surfactant at the same concentration in the range of 5-15% w/w, approximately, resulted in 22.41±1.81% w/w and 28.11±0.94% w/w for diuron, and 38.36±2.09% w/w and 39.28±5.71% w/w for diuron80, respectively. Results of control experiment (using water or calcium chloride solution.) were 11.82±1.34% and 11.91±1.79 for diuron and 23.59±3.49 and 24.09±2.20, respectively.

The highest leaching efficiency was obtained from the treatment with 20 CMC Triton X-100, similar to that soil column condition. According to the results, leaching efficiency of diuron- or diuron80-contaminated soil under shaking condition was comparatively less than those of soil column condition (approximated 5-20% w/w) in almost conditions tested.

Table 4.7 Leaching of 1-month diuron- and diuron80-aged soil under a shaking condition using organic solvent.

Organic solvent	Leaching of diuron from soil	
	Diuron (% w/w)	Diuron80 (% w/w)
Methanol (1% v/v)	17.03±2.55	30.82±3.93
Methanol (5% v/v)	21.07 ±2.72	34.89±3.89
Methanol (10% v/v)	27.80±2.12	39.72±0.99
Ethanol (1% v/v)	15.76±2.33	27.97±3.44
Ethanol (5% v/v)	22.48±1.93	30.94±3.15
Ethanol (10% v/v)	29.43±1.97	36.05±4.44
n-Butanol (1% v/v)	17.03±2.54	33.82±4.74

n-Butanol (5% v/v)	27.51±2.57	40.63±3.06
n-Butanol (10% v/v)	37.03±0.99	48.83±3.34
sec-Butanol (1% v/v)	27.60±1.48	31.33±4.30
sec-Butanol (5% v/v)	27.23±1.59	33.40±2.85
sec-Butanol (10% v/v)	30.00±1.51	39.51±0.81
Toluene (1% v/v)	26.41±1.12	34.86±4.13
Benzene (1% v/v)	26.04±2.97	36.20±5.98
Acetone (1% v/v)	26.97±2.39	33.04±2.62
Water	11.82±1.34	23.59±3.49
0.01 M $CaCl_2$	11.91±1.79	24.09±2.20

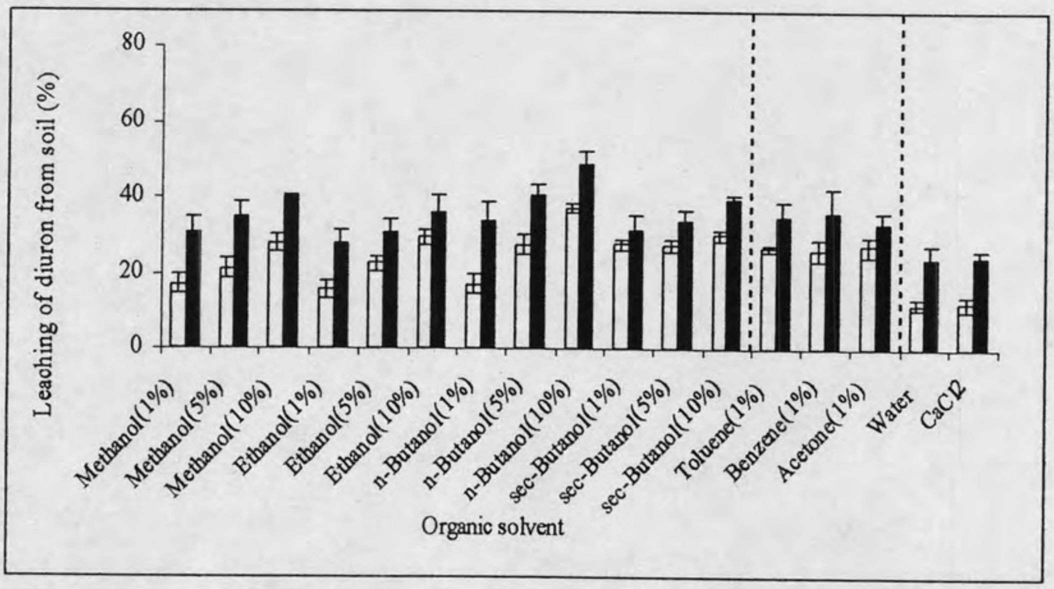


Figure 4.10 Leaching of 1-month diuron-aged soil (□) and 1-month diuron80-aged soil (■) under a shaking condition using organic solvents. The concentration is shown in bracket. (These results are the mean of 6 individual experiments)

Table 4.8 Leaching of 1-month diuron- and diuron80-aged soil under a shaking condition using surfactant.

Surfactant	Leaching of diuron from soil	
	Diuron (% w/w)	Diuron80 (% w/w)
Triton X-100 (1 CMC)	19.25±0.81	34.05±4.27
Triton X-100 (2 CMC)	17.71±0.32	29.66±2.04
Triton X-100 (8 CMC)	21.01±2.00	35.60±3.51
Triton X-100 (20 CMC)	25.55±2.00	40.39±2.97
Tergitol NP10 (1 CMC)	18.13±1.87	31.60±2.71
Tergitol NP10 (2 CMC)	18.86±1.20	30.74±2.67
Tergitol NP10 (8 CMC)	17.90±0.42	29.01±1.42
Tergitol NP10 (20 CMC)	20.83±0.97	33.66±0.86
Tween80 (1 CMC)	19.02±2.45	31.61±1.88
Tween80 (2 CMC)	17.70±1.80	26.51±4.42
Tween80 (8 CMC)	19.02±1.71	31.54±4.73
Tween80 (20 CMC)	23.58±1.46	36.06±2.82
Brij35 (1 CMC)	17.83±2.68	28.63±3.28
Brij35 (2 CMC)	16.52±1.52	25.90±2.66
Brij35 (8 CMC)	17.32±1.56	29.15±2.70
Brij35 (20 CMC)	20.77±0.93	34.26±2.89
SDS (1 CMC)	22.41±1.81	38.36±2.09

SDS (2 CMC)	28.11±0.94	39.28±5.71
Water	11.82±1.34	23.59±3.49
0.01 M $CaCl_2$	11.91±1.79	24.09±2.20

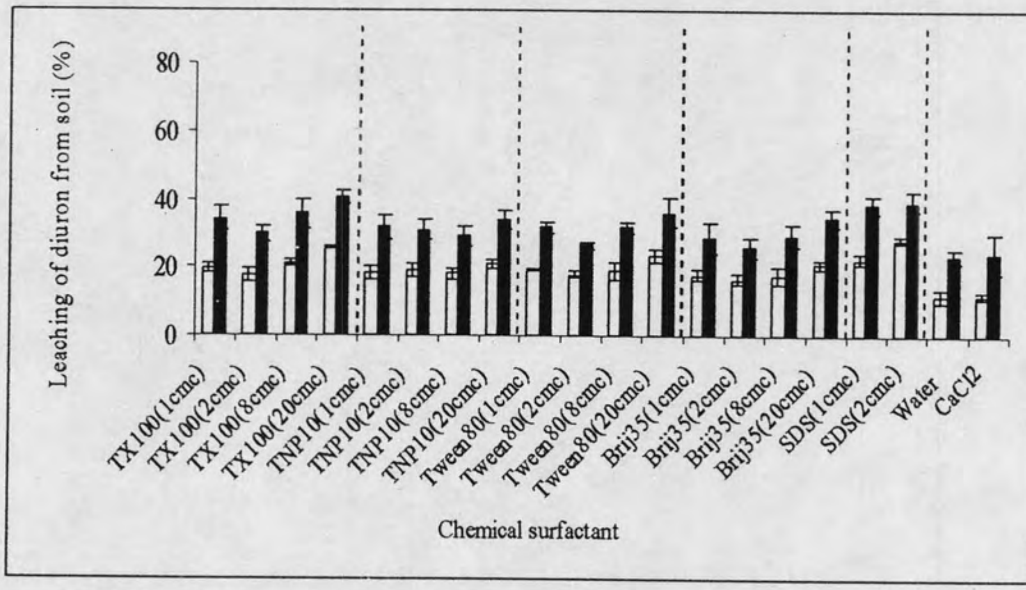


Figure 4.11 Leaching of 1-month diuron-aged soil (□) and 1-month diuron80-aged soil (■) under a shaking condition using chemical surfactants. The concentration is shown in bracket. (These results are the mean of 6 individual experiments)

Results 4.4.2 and 4.4.3 suggested that *n*-butanol and Triton X-100 are suitable organic solvent and surfactant, respectively, because they exhibited highest leaching efficiency when compared to other organic solvents and surfactants. Therefore, *n*-butanol and Triton X-100 were used for further experiments.

4.4.4 Effect of combination of suitable organic solvent and surfactant

From prior experiment results (Figure 4.10 to Figure 4.11), *n*-butanol is the organic solvent to leach diuron showing highest leaching efficiency, while Triton X-100 is the surfactant which has highest leaching efficiency. Therefore, to enhance the leaching efficiency, the combination of *n*-butanol and Triton X-100 for diuron leaching was investigated. Higher concentration of *n*-butanol was avoided due to its toxicity at higher concentration. According to the toxicity reason and result (Figure 4.7 and 4.10) showing that 10% (v/v) of *n*-butanol exhibited the highest leaching efficiency, *n*-butanol concentration was fixed at 10% (v/v) in the combination experiment. According to the results using combination of *n*-butanol and Triton X-100, both diuron and diuron80 could be leached from soil to different extent when 10% (v/v) of *n*-butanol and different concentrations of Triton X-100 were applied under either static or shaking conditions. The leaching of diuron contaminated in soil was then studied in more details using the combination of suitable organic solvents and surfactants. The leaching efficiency of diuron from soil by combination of organic solvent and surfactant in soil column was summarized in Figure 4.12 and Table 4.9, under a shaking condition in Figure 4.13 and Table 4.10, respectively.

In soil column condition, leaching efficiency of diuron and diuron80 was observed when the combination of 10% (v/v) *n*-butanol and Triton X-100 at various concentrations (1, 2 8 and 20 CMC). The results were not different for diuron leaching efficiency. However, leaching efficiency of diuron80 was slightly increased with increasing of Triton X-100 concentration (1, 2 and 8 CMC), except increasing to 20 CMC. Leaching efficiency of diuron80 was 74.01±1.66% w/w, 76.00±1.61% w/w and 81.01±3.04% w/w when Triton X-100 concentration is 1, 2 and 8 CMC, respectively.

Under shaking condition, leaching efficiency of diuron and diuron80 was observed when the combination of *n*-butanol 10% (v/v) *n*-butanol and Triton X-100 at various concentrations (1, 2 8 and 20 CMC). The results show slightly increasing when Triton X-100 concentration was increased (1, 2 and 8 CMC), except increasing to 20 CMC. Leaching efficiency of diuron were 36.43±2.10% w/w, 36.86±2.11% w/w and 40.15±1.72% w/w when Triton X-100 concentration is 1, 2 and 8 CMC, respectively. Leaching efficiency of diuron80 were 47.17±4.47% w/w, 48.01±4.41% w/w and 53.65±2.54% w/w when Triton X-100 concentration is 1, 2 and 8 CMC, respectively.

Leaching efficiency of diuron was not significantly improved with increasing of Triton X-100 concentration (1, 2, 8 and 20 CMC) which was combined with 10% (v/v) *n*-butanol, while the results of leaching of diuron80 showed slightly increasing of leaching efficiency when Triton X-100 at the concentration of 1, 2 and 8 CMC was combined with 10% (v/v) *n*-butanol. However, according to the results, it was proved that the combination of *n*-butanol (10% v/v) and Triton X-100 (at various concentrations) did enhance the leaching efficiency of either diuron or diuron80 compared to that when *n*-butanol or Triton X-100 was used alone. The leaching improvement was found to be in the range of 2-21% w/w for diuron and 5-44% w/w for diuron80.

Table 4.9 Leaching of 1-month diuron- and diuron80-aged soil packed in soil column using combination of *n*-butanol (10% v/v) and Triton X-100 (at various concentration; 1, 2, 8 and 20 cmc).

combination of *n*-butanol and Triton X-100	Leaching of diuron from soil	
	Diuron (% w/w)	Diuron80 (% w/w)
n-Butanol (10% v/v) + Triton X-100 (1 CMC)	49.78±2.40	74.01±1.66
n-Butanol (10% v/v) + Triton X-100 (2 CMC)	50.15±2.76	76.00±1.61
n-Butanol (10% v/v) + Triton X-100 (8 CMC)	52.46±3.26	81.01±3.40
n-Butanol (10% v/v) + Triton X-100 (20 CMC)	52.93±2.11	80.22±3.85

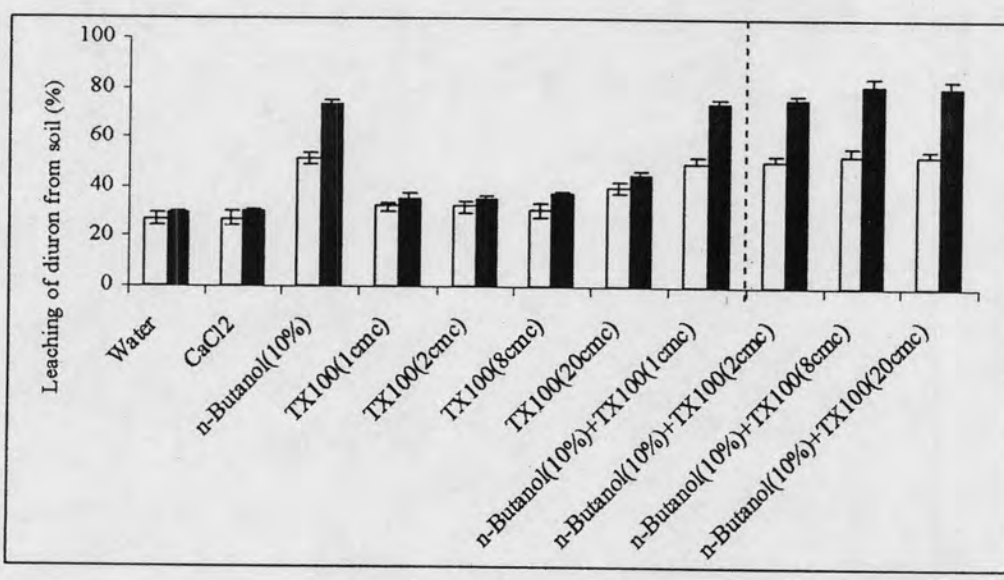


Figure 4.12 Leaching of 1-month diuron-aged soil (□) and 1-month diuron80-aged soil (■) packed in soil column using combination of *n*-butanol (10% v/v) and Triton X-100 (at various concentration). The concentration is shown in bracket. (These results are the mean of 6 individual experiments)

Table 4.10 Leaching of 1-month diuron- and diuron80-aged soil under shaking condition using combination of *n*-butanol (10% v/v) and Triton X-100 (at various concentration; 1, 2, 8 and 20 cmc).

combination of *n*-butanol and Triton X-100	Leaching of diuron from soil	
	Diuron (% w/w)	Diuron80 (% w/w)
n-Butanol (10% v/v) + Triton X-100 (1 CMC)	36.43±2.10	47.17±4.47
n-Butanol (10% v/v) + Triton X-100 (2 CMC)	36.86±2.11	48.01±4.41
n-Butanol (10% v/v) + Triton X-100 (8 CMC)	40.15±1.72	53.65±2.54
n-Butanol (10% v/v) + Triton X-100 (20 CMC)	39.56±2.07	49.48±3.39

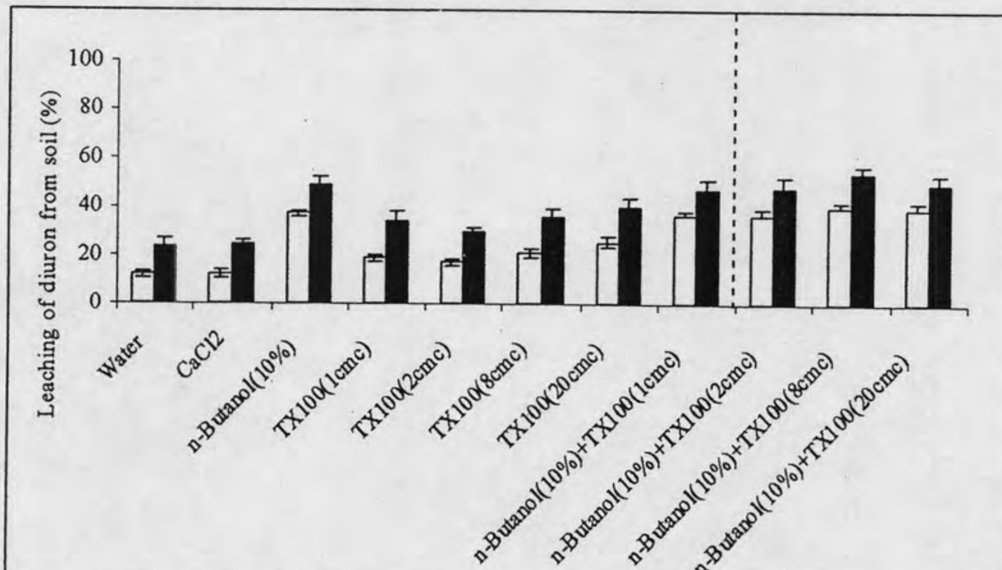


Figure 4.13 Leaching of 1-month diuron-aged soil (□) and 1-month diuron80-aged soil (■) under a shaking condition using combination of *n*-butanol (10% v/v) and Triton X-100 (at various concentration). The concentration is shown in bracket. (These results are the mean of 6 individual experiments)

4.4.5 Effect of pH on leaching of diuron in soil

Since diuron is nearly at neutral pH, it is expected that no significant effect of pH would be discovered due to the negligible protonation effects (Chaplain et al., 2001). However, change of soil pH may be influenced on adsorption and effect to soil and solution in soil washing experiment. Therefore, it is necessary to investigate effect of pH on leaching of diuron contaminated in soil. Since the initial pH of soil and leachate is approximately at pH 7.0, the investigation was performed at 1 pH unit difference (pH 6 and pH 8). The solutions were prepared and used to adjust soil pH to pH 6 and pH 8 to evaluate the effect of soil pH on diuron leaching (Figure 4.14, 4.15 and Table 4.11, 4.12).

According to previous results, leaching efficiency in soil column using 10% (v/v) *n*-butanol (soil pH 7) were 50.99±2.32% w/w for diuron and 72.95±1.70% w/w for diuron80. When soil was pre-equilibrated to pH 6 before the leaching, the leaching efficiency using 10% (v/v) *n*-butanol in soil column were decreased to 42.56±2.53% w/w for diuron and 65.50±2.39% w/w for diuron80. When soil was pre-equilibrated to pH 8 before the leaching, the leaching efficiency using 10% (v/v) *n*-butanol in soil column were 49.41±2.48% w/w for diuron and 72.39±1.34% w/w for diuron80, respectively.

The results of leaching efficiency under shaking condition using *n*-butanol 10% (v/v) *n*-butanol (soil pH 7) were 37.08±0.99% w/w for diuron and 48.83±3.34% w/w for diuron80. When soil was pre-equilibrated to pH 6 before the leaching, the leaching efficiency using 10% (v/v) *n*-butanol in soil column were decreased to 33.86±1.57% w/w for diuron and 47.44±3.87% w/w for diuron80. When soil was pre-equilibrated to pH 8 before the leaching, the leaching efficiency using 10% (v/v) *n*-

butanol in soil column were 37.09±1.87% w/w for diuron and 48.47±2.17% w/w for diuron80, respectively.

These results show decreasing of leaching efficiency using 10% (v/v) *n*-butanol approximated 3-9% w/w for diuron and 2-5% w/w for diuron80 when soil was pre-equilibrated to pH 6 before the leaching, while the results show insignificant different of leaching efficiency using 10% (v/v) *n*-butanol when soil was pre-equilibrated to pH 8 compared with that when soil at pH 7 (control).

The results of leaching efficiency in soil column using 20 CMC Triton X-100 (soil pH 7) were 39.68±2.73% w/w for diuron and 45.07±1.19% w/w for diuron80. When soil was pre-equilibrated to pH 6 before the leaching, the leaching efficiency using 10% (v/v) *n*-butanol in soil column was decreased to 33.63±1.59% w/w for diuron and 37.66±1.36% w/w for diuron80. When soil was pre-equilibrated to pH 8 before the leaching, the leaching efficiency using 10% (v/v) *n*-butanol in soil column were increased to 41.35±3.13% w/w for diuron and 47.39±0.41% w/w for diuron80, respectively.

The results of leaching efficiency under shaking condition using 20 CMC Triton X-100 (soil pH 7) were 25.55±2.00% w/w for diuron and 40.39±2.97% w/w for diuron80. When soil was pre-equilibrated to pH 6 before the leaching, the leaching efficiency using 10% (v/v) *n*-butanol in soil column were decreased to 22.00±0.36% w/w for diuron and 31.75±1.70% w/w for diuron80. When soil was pre-equilibrated to pH 8 before the leaching, the leaching efficiency using 10% (v/v) *n*-butanol in soil column were increased to 27.52±2.54% w/w for diuron and 40.43±0.38% w/w for diuron80, respectively.

These results show decreasing of leaching efficiency using 20 CMC Triton X-100 approximated 4-6% w/w for diuron and 7-9% w/w for diuron80 when soil was pre-equilibrated to pH 6 before the leaching, while the results show insignificant different of leaching efficiency using 20 CMC Triton X-100 when soil was pre-equilibrated to pH 8 compared with that when soil at pH 7 (control). This trend is similar to that using 10% (v/v) *n*-butanol.

According to the results, it indicated that low pH influenced the decreasing of leaching efficiency of diuron and diuron80 from soil.

Table 4.11 Leaching of 1-month diuron- and diuron80-aged soil packed in soil column using *n*-butanol and Triton X-100 after adjust pH.

Organic solvent and surfactant at various pH	Leaching of diuron from soil	
	Diuron (% w/w)	Diuron80 (% w/w)
n-Butanol (10% v/v) pH6	42.56±2.53	65.50±2.39
n-Butanol (10% v/v) pH7	50.99±2.32	72.95±1.70
n-Butanol (10% v/v) pH8	49.41±2.48	72.39±1.34
Triton X-100 (20 CMC) pH6	33.63±1.59	37.66±1.36
Triton X-100 (20 CMC) pH7	39.68±2.73	45.07±1.19
Triton X-100 (20 CMC) pH8	41.35±3.13	47.39±0.41

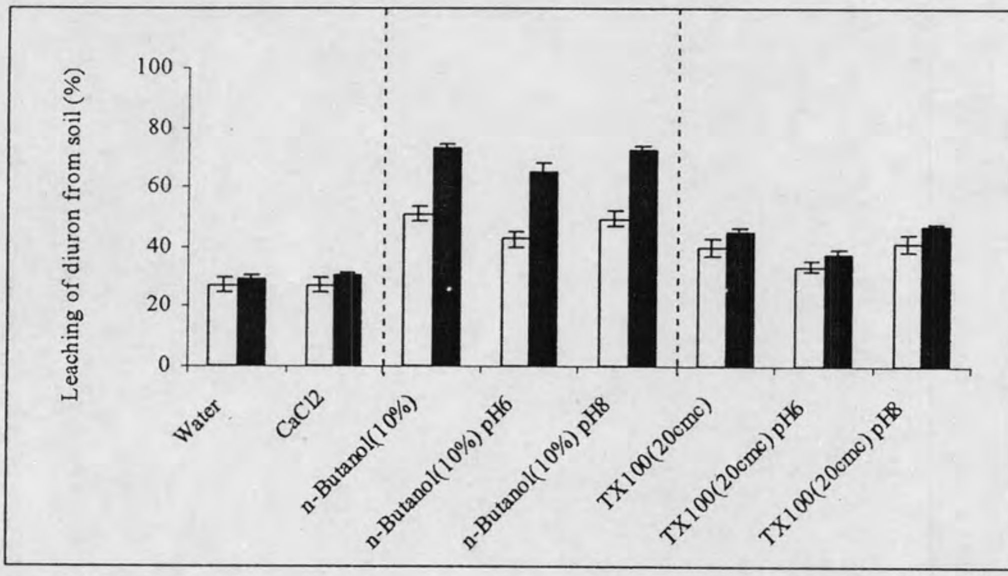


Figure 4.14 Leaching of 1-month diuron-aged soil (□) and 1-month diuron80-aged soil (■) packed in soil column using *n*-butanol and Triton X-100 after adjust pH. The concentration is shown in bracket. (These results are the mean of 6 individual experiments)

Table 4.12 Leaching of 1-month diuron- and diuron80-aged soil under shaking condition using *n*-butanol and Triton X-100 after adjust pH.

Organic solvent and surfactant at various pH	Leaching of diuron from soil	
	Diuron (% w/w)	Diuron80 (% w/w)
n-Butanol (10% v/v) pH6	33.86±1.57	47.44±3.87
n-Butanol (10% v/v) pH7	37.03±0.99	48.83±3.34
n-Butanol (10% v/v) pH8	37.09±1.87	48.47±2.17
Triton X-100 (20 CMC) pH6	22.00±0.36	31.75±1.70
Triton X-100 (20 CMC) pH7	23.58±1.46	36.02±2.82
Triton X-100 (20 CMC) pH8	27.52±2.54	40.43±0.38

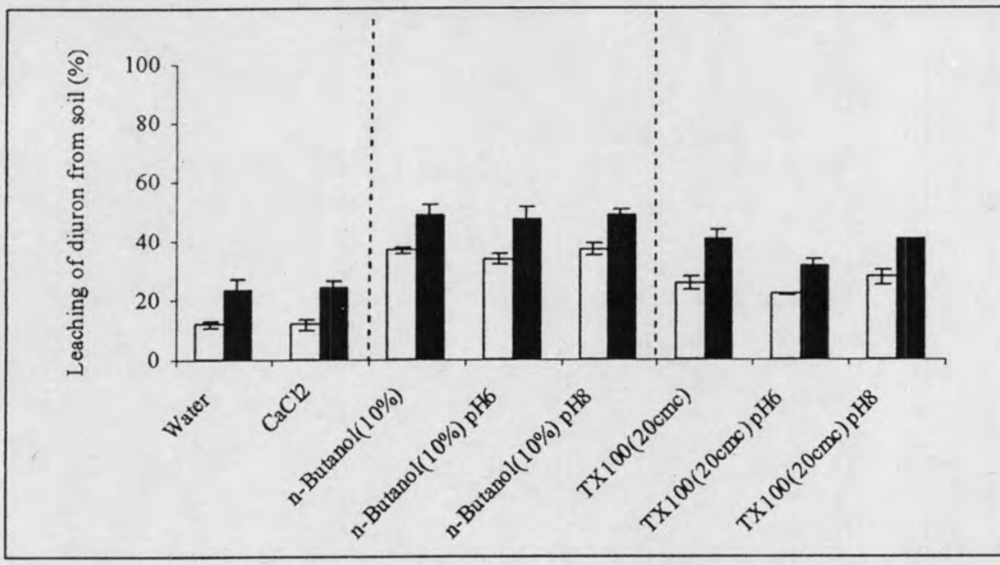


Figure 4.15 Leaching of 1-month diuron-aged soil (□) and 1-month diuron80-aged soil (■) under a shaking condition using *n*-butanol and Triton X-100 after adjust pH. The concentration is shown in bracket. (These results are the mean of 6 individual experiments)

4.4.6 Effect of ionic strength (μ) on leaching of diuron in soil

Another factor that may be affected diuron leaching was ionic strength (μ). To investigate the effects of the ionic strength and its role in the leaching of diuron from soil, tests were conducted at low (μ 0.03 M) and high (μ 0.15 M and 0.3 M) ionic strength. Calculation of ionic strength as follow;

$$CaCl_2 \longrightarrow Ca^{2+} + 2\,Cl^{-1}$$

$$\text{Ionic strength of 0.01 M } CaCl_2 = \tfrac{1}{2}\Sigma C_i Z_i^2$$

$$= \tfrac{1}{2}[(0.01).(2)^2+(0.01).(-1)^2]$$

$$= 0.03$$

Where; C_i is the concentration of the ith ion concentration.

Z_i is the valence facter (charge)

The summation, Σ, is taken over all the possible ions in the solution.

The results of effect of ionic strength on leaching are shown in Figure 4.16 and Table 4.13 for packed soil column condition and Figure 4.17 and Table 4.14 for shaking condition, respectively.

According to previous results, leaching efficiency in soil column using *n*-butanol 10% (v/v) after pre-equilibrated using 0.01 M $CaCl_2$ (μ 0.03 M; control experiment) were 50.99±2.32% w/w for diuron and 72.95±1.70% w/w for diuron80. When soil was pre-equilibrated using 0.05 M $CaCl_2$ (μ 0.15 M) before the leaching, leaching efficiency using 10% (v/v) *n*-butanol in soil column were decreased to 38.40±2.30% w/w for diuron and 69.92±1.60% w/w for diuron80. When soil was pre-equilibrated using 0.1 M $CaCl_2$ (μ 0.3 M), leaching efficiency using 10% (v/v) *n*-butanol in soil column were decreased to 35.30±0.74% w/w for diuron and 66.55±0.52% w/w for diuron80, respectively.

Leaching efficiency under shaking condition using *n*-butanol 10% (v/v) after pretreated using 0.01 M $CaCl_2$ (μ 0.03 M; control experiment) were 37.03±0.99% w/w for diuron and 48.83±3.34% w/w for diuron80. When soil was pre-equilibrated using 0.05 M $CaCl_2$ (μ 0.15 M) before the leaching, leaching efficiency using 10% (v/v) *n*-butanol in soil column were decreased to 32.01±1.58% w/w for diuron and 43.50±4.55% w/w for diuron80. When soil was pre-equilibrated using 0.1 M $CaCl_2$ (μ 0.3 M) before the leaching, leaching efficiency using 10% (v/v) *n*-butanol in soil column were decreased to 29.16±2.19% w/w for diuron and 40.80±3.69% w/w for diuron80, respectively.

These results show leaching efficiency of diuron and diuron80 using 10% (v/v) *n*-butanol was decreased with increasing of ionic strength (from 0.03 to 0.15 and

0.3 M). The decreasing was found to be in the range of 5-16% w/w for diuron and 3-8% w/w for diuron80.

Leaching efficiency in soil column using 20 CMC Triton X-100 after pretreated using 0.01 M $CaCl_2$ (μ 0.03 M; control experiment) were 39.68±2.73% w/w for diuron and 45.07±1.19% w/w for diuron80. When soil was pre-equilibrated using 0.05 M $CaCl_2$ (μ 0.15 M) before the leaching, leaching efficiency using 20 CMC Triton X-100 in soil column were decreased to 38.08±0.89% w/w for diuron and 47.79±1.75% w/w for diuron80. When soil was pre-equilibrated using 0.1 M $CaCl_2$ (μ 0.3 M), leaching efficiency using 20 CMC Triton X-100 in soil column were decreased to 37.15±0.68% w/w for diuron and 46.48±2.82% w/w for diuron80, respectively.

Leaching efficiency under shaking condition using 20 CMC Triton X-100 after pretreated using 0.01 M $CaCl_2$ (μ 0.03 M; control experiment) were 25.55±2.00% w/w for diuron and 40.39±2.97% w/w for diuron80. When soil was pre-equilibrated using 0.05 M $CaCl_2$ (μ 0.15 M) before the leaching, leaching efficiency using 20 CMC Triton X-100 in soil column were decreased to 27.44±1.80% w/w for diuron and 37.07±0.49% w/w for diuron80. When soil was pre-equilibrated using 0.1 M $CaCl_2$ (μ 0.3 M), leaching efficiency using 20 CMC Triton X-100 in soil column were decreased to 26.42±1.11% for diuron and 36.80±1.23% for diuron80, respectively. The results suggested that ionic strength influenced the leaching of diuron and diuron80 from soil.

These results show insignificant different of leaching efficiency of diuron and diuron80 using 20 CMC Triton X-100 when ionic strength was increased (from 0.03 to 0.15 and 0.3 M).

According to the results, its suggested that ionic strength influenced the decreasing of leaching efficiency of diuron and diuron80 from soil using 10% (v/v) *n*-butanol but not for that using 20 CMC Triton X-100.

Table 4.13 Leaching of 1-month diuron- and diuron80-aged soil packed in soil column condition using *n*-butanol and Triton X-100 after adjust ionic strength.

Organic solvent and surfactant at various ionic strength	Leaching of diuron from soil	
	Diuron (% w/w)	Diuron80 (% w/w)
n-Butanol (10% v/v) 0.01 M $CaCl_2$	50.99±2.32	72.95±1.70
n-Butanol (10% v/v) 0.05 M $CaCl_2$	38.40±2.30	69.92±1.60
n-Butanol (10% v/v) 0.1 M $CaCl_2$	35.30±0.74	66.55±0.52
Triton X-100 (8 CMC) 0.01 M $CaCl_2$	39.68±2.73	45.07±1.19
Triton X-100 (8 CMC) 0.05 M $CaCl_2$	38.08±0.89	47.79±1.75
Triton X-100 (20 CMC) 0.1 M $CaCl_2$	37.15±0.68	46.48±2.82

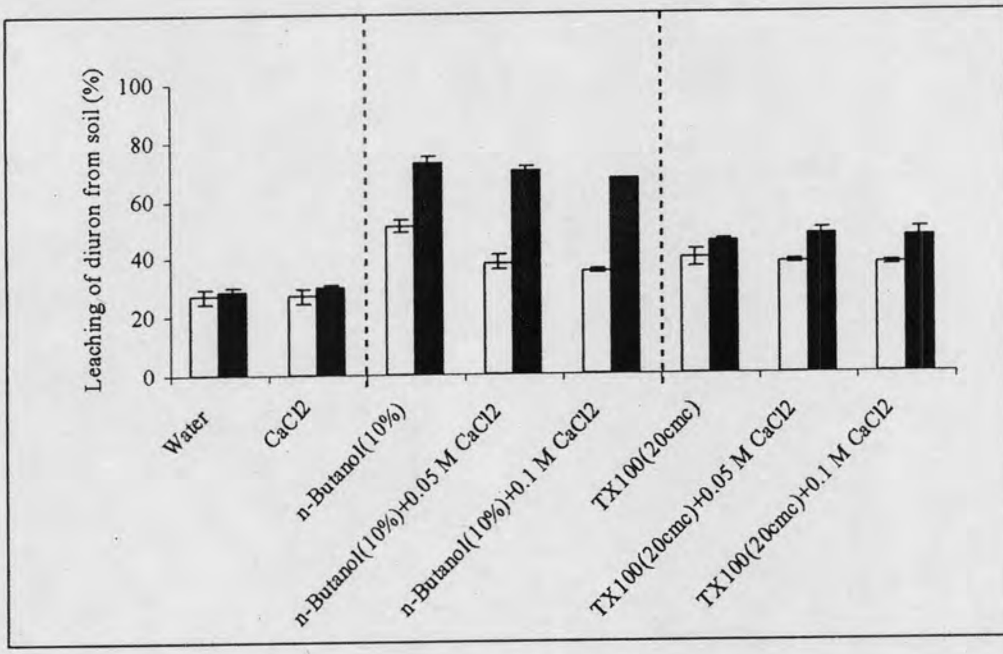


Figure 4.16 Leaching of 1-month diuron-aged soil (□) and 1-month diuron80-aged soil (■) packed in soil column using *n*-butanol and Triton X-100 after adjust ionic strength. The concentration is shown in bracket. (These results are the mean of 6 individual experiments)

Table 4.14 Leaching of 1-month diuron- and diuron80-aged soil under shaking condition using *n*-butanol and Triton X-100 after adjust ionic strength.

Organic solvent and surfactant at various ionic strength	Leaching of diuron from soil	
	Diuron (% w/w)	Diuron80 (% w/w)
n-Butanol (10% v/v) 0.01 M $CaCl_2$	37.03±0.99	48.83±3.34
n-Butanol (10% v/v) 0.05 M $CaCl_2$	32.01±1.58	43.50±4.55
n-Butanol (10% v/v) 0.1 M $CaCl_2$	29.16±2.19	40.80±3.69
Triton X-100 (20 CMC) 0.01 M $CaCl_2$	25.55±2.00	40.39±2.97
Triton X-100 (20 CMC) 0.05 M $CaCl_2$	27.44±1.80	37.07±0.49
Triton X-100 (20 CMC) 0.1 M $CaCl_2$	26.42±1.11	36.80±1.23

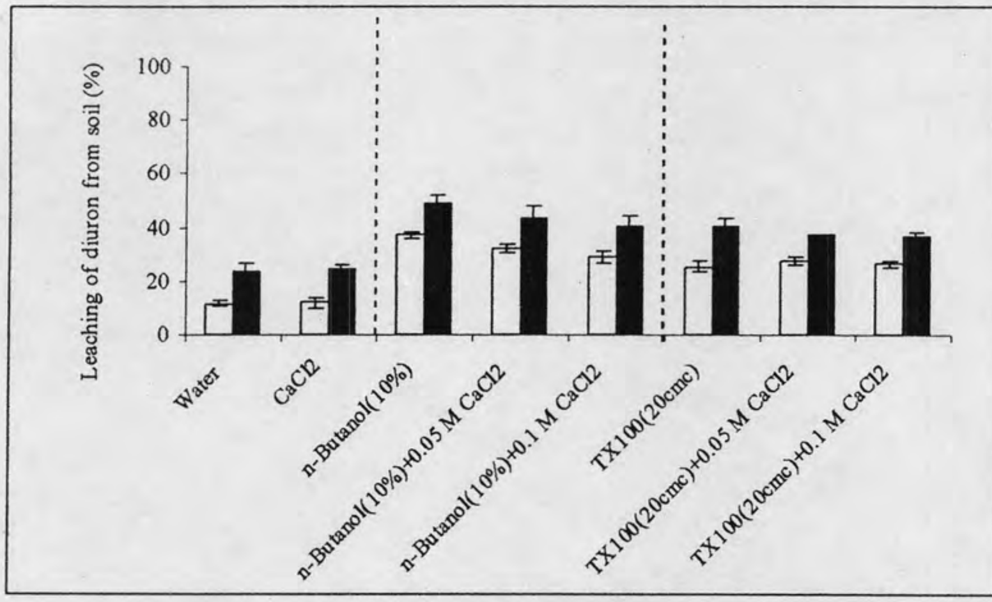


Figure 4.17 Leaching of 1-month diuron-aged soil (□) and 1-month diuron80-aged soil (■) under a shaking condition using *n*-butanol and Triton X-100 after adjust ionic strength. The concentration is shown in bracket. (These results are the mean of 6 individual experiments)

4.5 Photodegradation of Diuron

Diuron is a pollutant that has been the subject of the environmental concern because of its low biodegradability, chemical stability and low solubility. Since it can slowly penetrate through soil and contaminates underground water, organic solvent and surfactant have been proposed for use in soil washing and pump-and-treat technologies to assist the solubilization of sorbed hydrophobic contaminants. The leachated diuron solution would then be further treated using the process of photolysis (Chan and Chu, 2005). In this experiment, titania synthesized according to the work of Klongdee and coworker (Klongdee et al., 2005) was employed as a catalyst in the photodegradation of diuron and diuron80 (UV/TiO_2 system). Photocatalytic degradation of diuron and diuron80 in 1 g.l^{-1} TiO_2 suspension was investigated using UV lamps (Phillips Cleo 15 W). Photocatalytic samples were fraction of leachate diuron from soil column after the pretreatment with calcium chloride solution (F5) as well as fraction of diuron leached from soil with 5-10 column volume of organic solvent or surfactant (F6-F10) as described in Method 3.8 (Figure 3.8). Rate of photooxidation was simplified to the apparent first-order kinetics, according to Langmuir-Hinshelwood kinetics model (Konstantinou and Albanis, 2003). Therefore, the plot of ln (Co/C) versus time where Co is an initial diuron concentration of the leachate and C is concentration of diuron, was expected to be a straight line with the slope equal to the apparent rate constant, k_{app}, of the degradation. Figure 4.18-4.24 compares the photodegradation of diuron in solution leached from soil column using 10% (v/v) aqueous solution of various organic solvents (methanol, ethanol and *n*-butanol), aqeous solution containing 20 CMC surfactant (Triton X-100 and Tween80) or a control (water and calcium chloride solution). The photocatalytic reaction was initiated by exposing solution in test tubes to UV light (total 60 Watt) and the degradation was continuously monitored for 24 h. The photocatalytic reaction procedures and raw data were shown on Method 3.8 and Appendix D, respectively. Figure 4.24-4.31 shows the disappearance of diuron80 in the same degradation condition as that of diuron. Raw data was shown on Appendix D. Rate constants of the photocatalytic degradation reaction (k_{app}) and R-squared values (R^2) are shown in Table 4.15 and 4.16 for diuron, and Table 4.17 and 4.18 for diuron 80, respectively.

According to Figure 4.18-4.31 and Table 4.15-4.18., k_{app} of the fraction pretreated by calcium chloride solution (F5) for all experiments was 0.0210±0.0018 h^{-1} for diuron and 0.0251±0.0022 h^{-1} for diuron80, respectively. For the fractions leached from soil column using different solvent (F6-F10), the results shown same trend of degradation for both diuron and diuron80. R-squared values in Table 4.16 and 4.18 indicated tend to approach to first order kinetic reaction transform of degradation reaction. Nevertheless, the fraction leached from soil column with 10% (v/v) *n*-butanol solution (Figure 4.20 and 4.27) showed the highest rate of photocatalytic degradation in both diuron and diuron80, comparing to other solvents. When the F9 (9^{th} fraction) leached from soil column with 10% (v/v) *n*-butanol solution was photocatalytically treated, the highest rate of diuron (0.0552 h^{-1}) and diuron80 (0.0705 h^{-1}) degradation were obtained. The general trend for the rate of diuron degradation in the fraction of leachate using different solvent is as followed: *n*-butanol >> methanol and ethanol > Triton X-100, water and calcium chloride solution > Tween80. For diuron80, the trend is: *n*-butanol >> methanol > Triton X-100 > ethanol > Tween80 and water > calcium chloride solution.

Table 4.15 Rate constants of the photocatalytic degradation of diuron fractions leached from soil column using different solvent.

Solvent	k_{app} (h^{-1})					
	F5	F6	F7	F8	F9	F10
10% (v/v) Methanol	0.0209	0.0287	0.0230	0.0230	0.0166	0.0149
10% (v/v) Ethanol	0.0207	0.0210	0.0183	0.0177	0.0123	0.0133
10% (v/v) *n*-Butanol	0.0209	0.0503	0.0516	0.0473	0.0552	0.0520
20 CMC Triton X-100	0.0186	0.0187	0.0204	0.0163	0.0128	0.0151
20 CMC Tween80	0.0192	0.0081	0.0112	0.0089	0.0128	0.0132
Water	0.0223	0.0167	0.0125	0.0105	0.0115	0.0091
0.01 M $CaCl_2$	0.0241	0.0186	0.0173	0.0134	0.0111	0.0080

Table 4.16 R-squared values of rate constants of the photocatalytic degradation of diuron fractions leached from soil column using different solvent.

Solvent	R^2					
	F5	F6	F7	F8	F9	F10
10% (v/v) Methanol	0.9600	0.9801	0.9933	0.9986	0.9501	0.9760
10% (v/v) Ethanol	0.9374	0.9908	0.9406	0.9885	0.9965	0.9946
10% (v/v) *n*-Butanol	0.9761	0.9382	0.9854	0.9769	0.9824	0.9597
20 CMC Triton X-100	0.9910	0.9585	0.9445	0.9682	0.9894	0.9913
20 CMC Tween80	0.9597	0.9254	0.9964	0.9344	0.9732	0.9784
Water	0.9754	0.9955	0.9908	0.9904	0.9747	0.9742
0.01 M $CaCl_2$	0.9898	0.9759	0.9792	0.9854	0.9759	0.9601

Table 4.17 Rate constants of the photocatalytic degradation of diuron80 fractions leached from soil column using different solvent.

Solvent	k_{app} (h^{-1})					
	F5	F6	F7	F8	F9	F10
10% (v/v) Methanol	0.0249	0.0264	0.0241	0.0291	0.0203	0.0215
10% (v/v) Ethanol	0.0267	0.0242	0.0249	0.0230	0.0198	0.0237
10% (v/v) *n*-Butanol	0.0267	0.0557	0.0555	0.0612	0.0705	0.0666
20 CMC Triton X-100	0.0222	0.0269	0.0323	0.0256	0.0193	0.0224
20 CMC Tween80	0.0221	0.0227	0.0165	0.0144	0.0226	0.0199
Water	0.0260	0.0188	0.0181	0.0190	0.0186	0.0274
0.01 M $CaCl_2$	0.0272	0.0161	0.0134	0.0203	0.0217	0.0275

Table 4.16 R-squared values of rate constants of the photocatalytic degradation of diuron80 fractions leached from soil column using different solvent.

Solvent	R^2					
	F5	F6	F7	F8	F9	F10
10% (v/v) Methanol	0.9586	0.9557	0.9537	0.9794	0.9813	0.9943
10% (v/v) Ethanol	0.9832	0.9737	0.9786	0.9900	0.9963	0.9797
10% (v/v) *n*-Butanol	0.9707	0.9755	0.9737	0.9842	0.9968	0.9916
20 CMC Triton X-100	0.9839	0.9505	0.9975	0.9960	0.9560	0.9974
20 CMC Tween80	0.9332	0.9902	0.9825	0.9739	0.9834	0.9904
Water	0.9776	0.9489	0.9287	0.9892	0.9522	0.9607
0.01 M $CaCl_2$	0.9928	0.9565	0.9819	0.9804	0.9845	0.9956

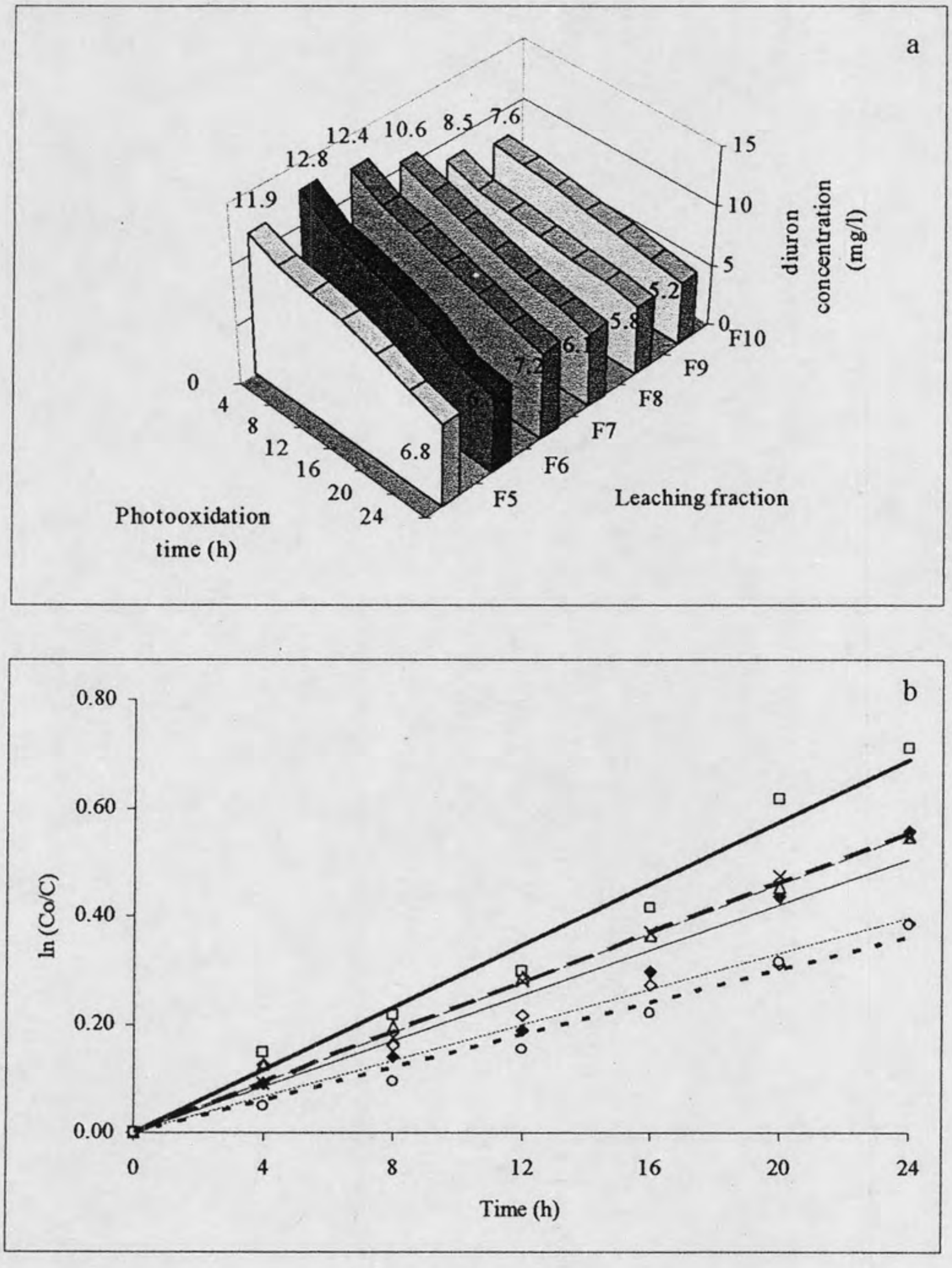


Figure 4.18 a) Photocatalytic degradation of diuron vs time of the final fraction (F5) that pretreated with calcium chloride solution and five fractions of leachate (F6-F10) using 10% (v/v) methanol b) First-order linear transforms of the degradation of diuron: (—◆—) F5, (—□—) (--△--) (— X —) (--◇--) (...○...) refer to F6-F10, respectively.

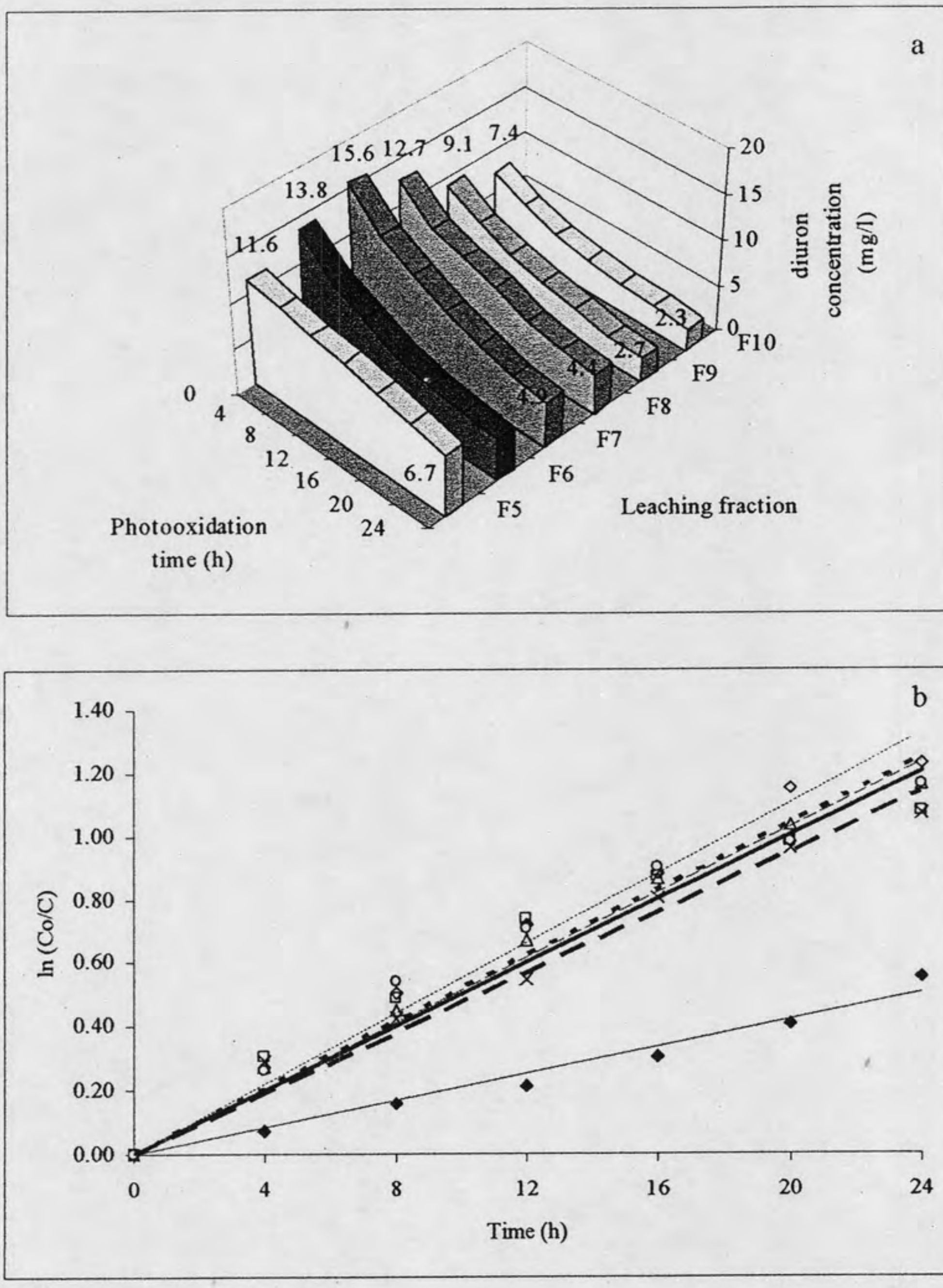
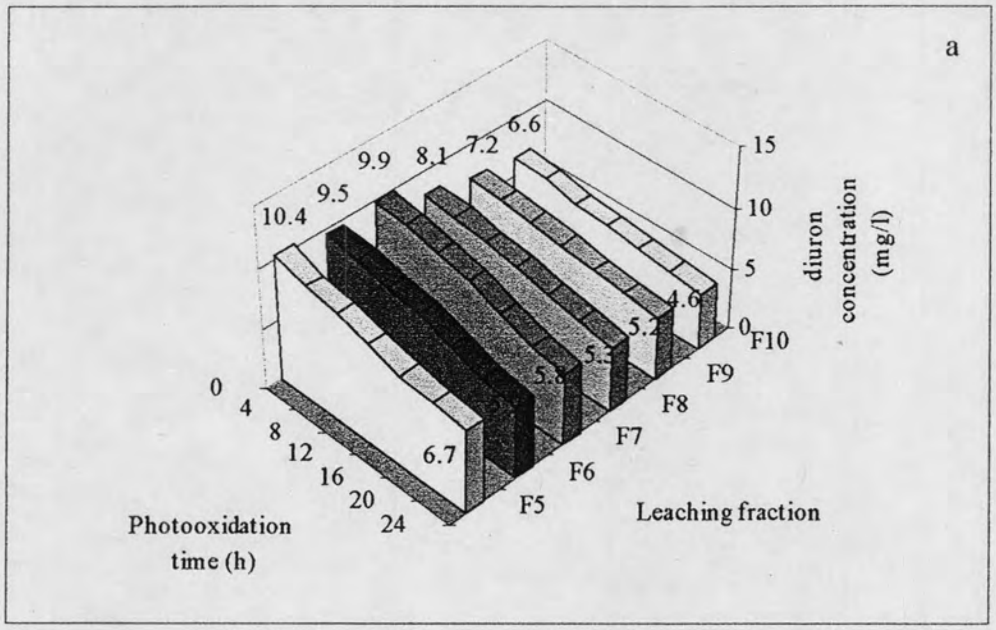


Figure 4.20 a) Photocatalytic degradation of diuron vs time of the final fraction (F5) that pretreated with calcium chloride solution and five fractions of leachate (F6-F10) using 10% (v/v) *n*-butanol b) First-order linear transforms of the degradation of diuron: (—◆—) F5, (—□—) (--△--) (— ✕ -) (--◇--) (...○..) refer to F6-F10, respectively.



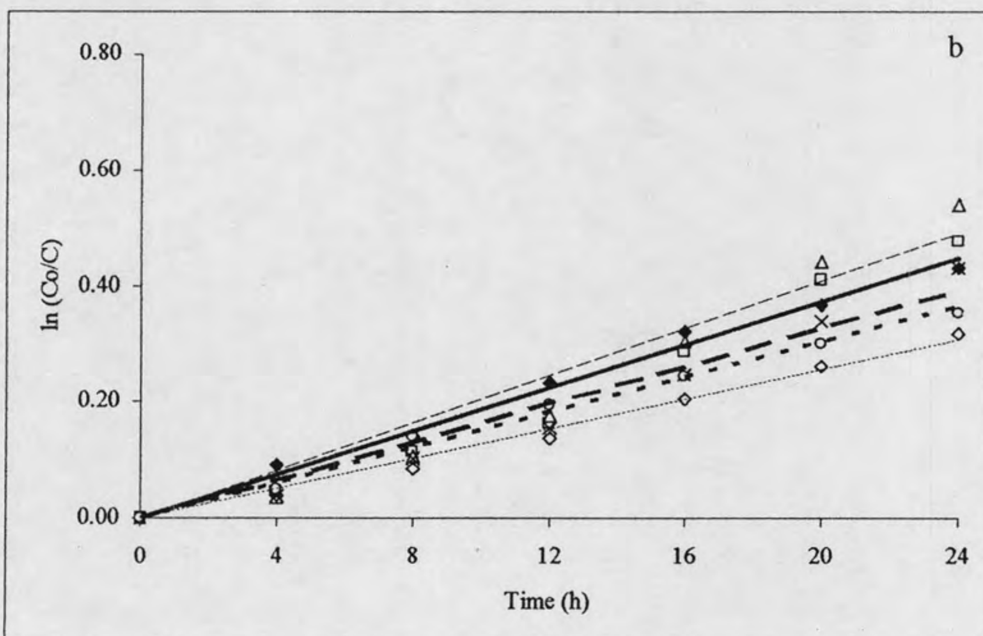


Figure 4.21 a) Photocatalytic degradation of diuron vs time of the final fraction (F5) that pretreated with calcium chloride solution and five fractions of leachate (F6-F10) using 20 CMC Triton X-100 b) First-order linear transforms of the degradation of diuron: (—◆—) F5, (—□—) (--△--) (— X —) (--◇--) (…○…) refer to F6-F10, respectively.

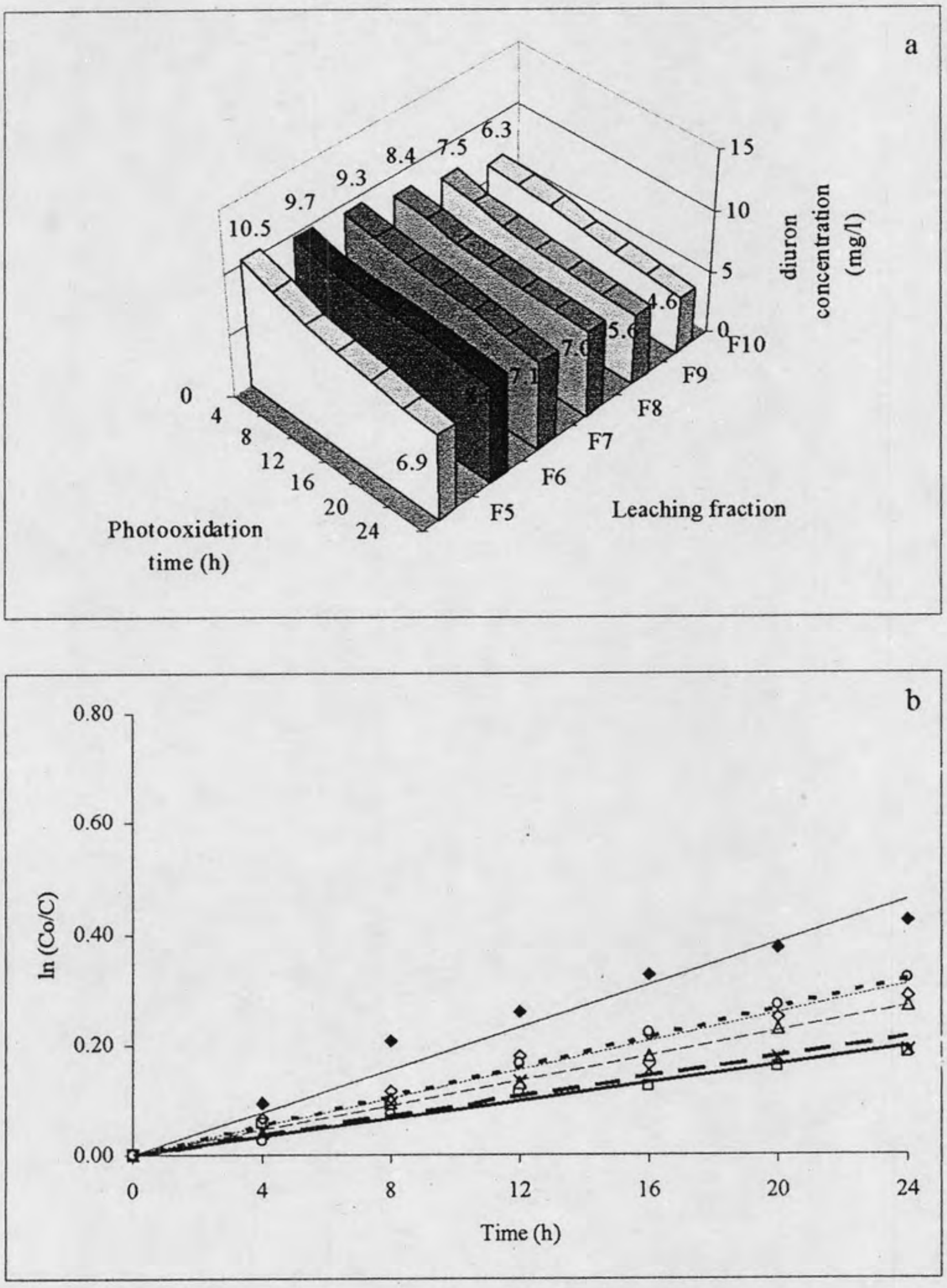
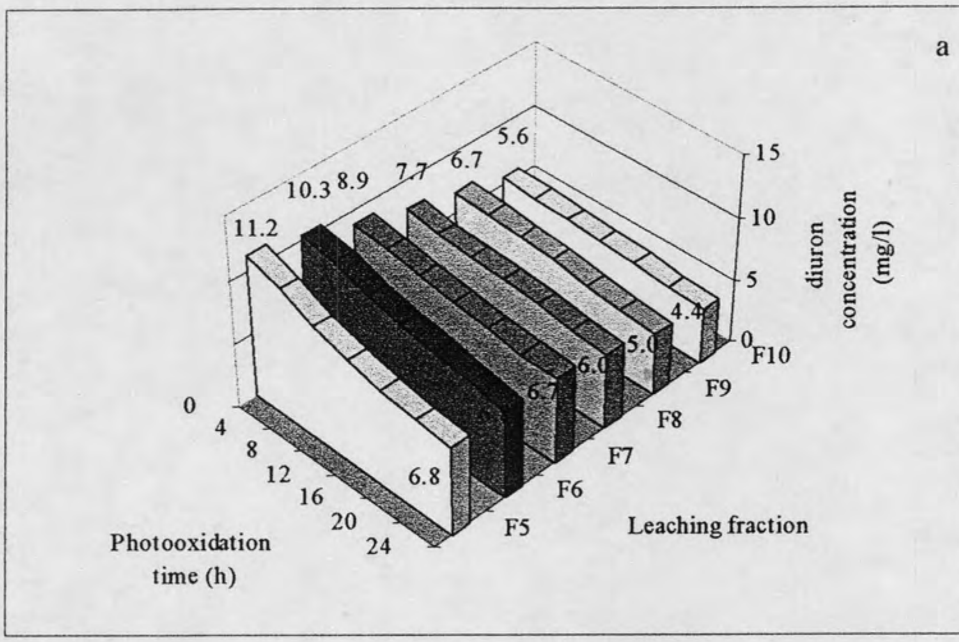


Figure 4.22 a) Photocatalytic degradation of diuron vs time of the final fraction (F5) that pretreated with calcium chloride solution and five fractions of leachate (F6-F10) using 20 CMC Tween80 b) First-order linear transforms of the degradation of diuron: (--◆--) F5, (—□—) (--△--) (— X —) (--◇--) (··○··) refer to F6-F10, respectively.



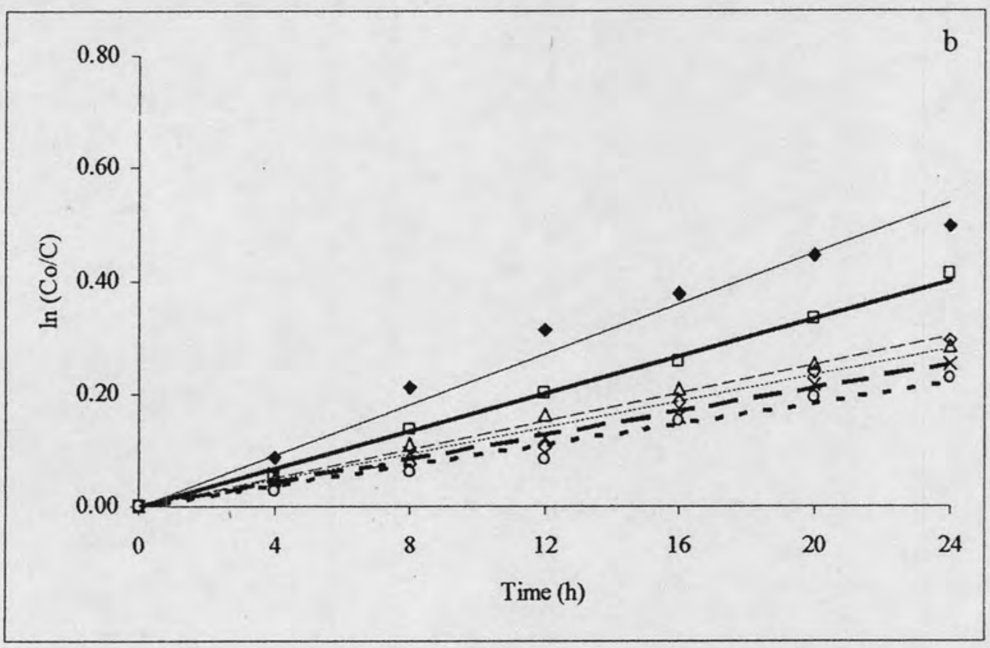


Figure 4.23 a) Photocatalytic degradation of diuron vs time of the final fraction (F5) that pretreated with calcium chloride solution and five fractions of leachate (F6-F10) using water b) First-order linear transforms of the degradation of diuron:

(--◆--) F5, (—□—) (--△--) (— X —) (--◇--) (...○...) refer to F6-F10, respectively.

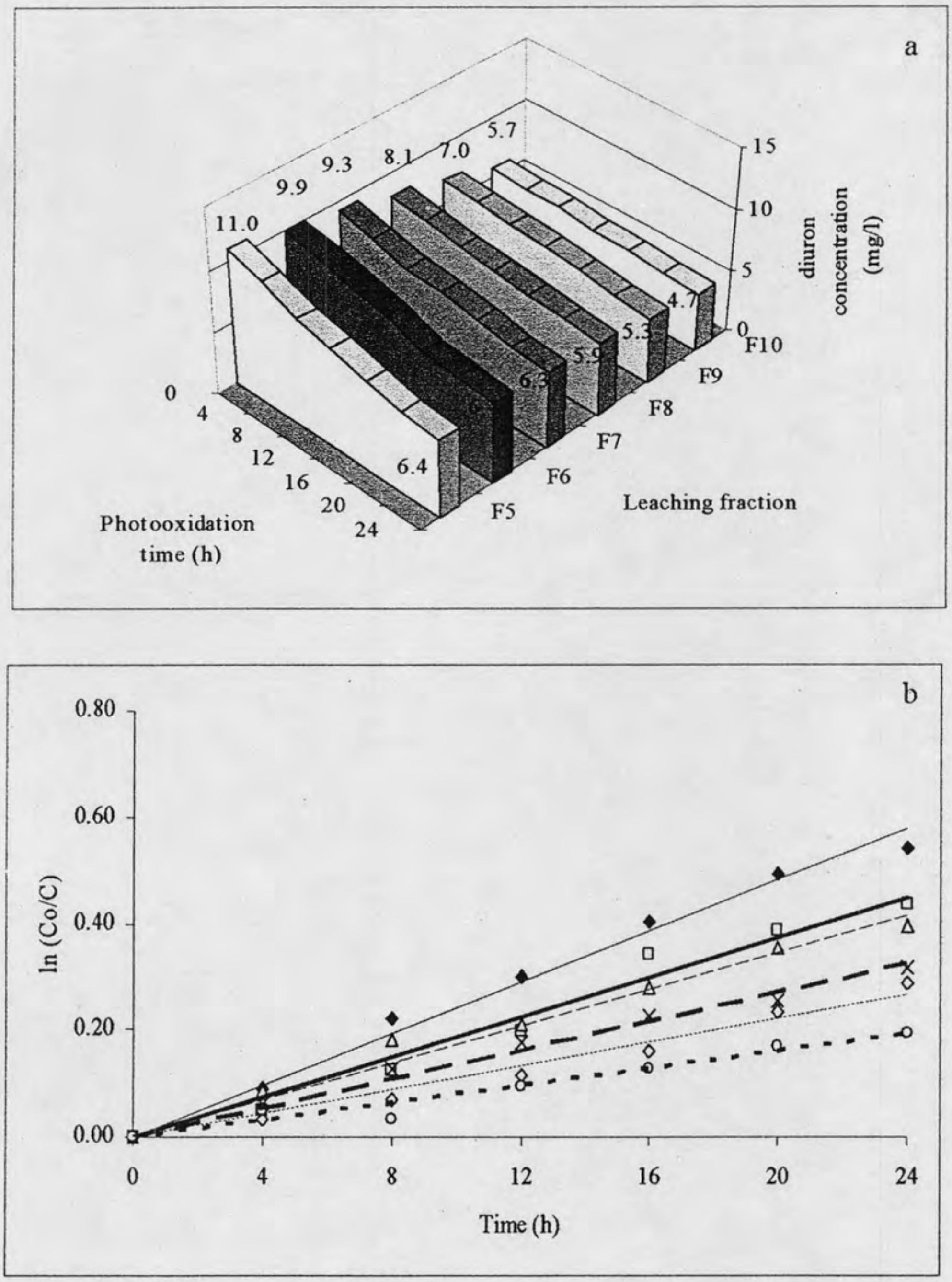


Figure 4.24 a) Photocatalytic degradation of diuron vs time of the final fraction (F5) that pretreated with calcium chloride solution and five fractions of leachate (F6-F10) using calcium chloride solution b) First-order linear transforms of the degradation of diuron: (—◆—) F5, (—□—) (--△--) (— X —) (--◇--) (···○···) refer to F6-F10, respectively.

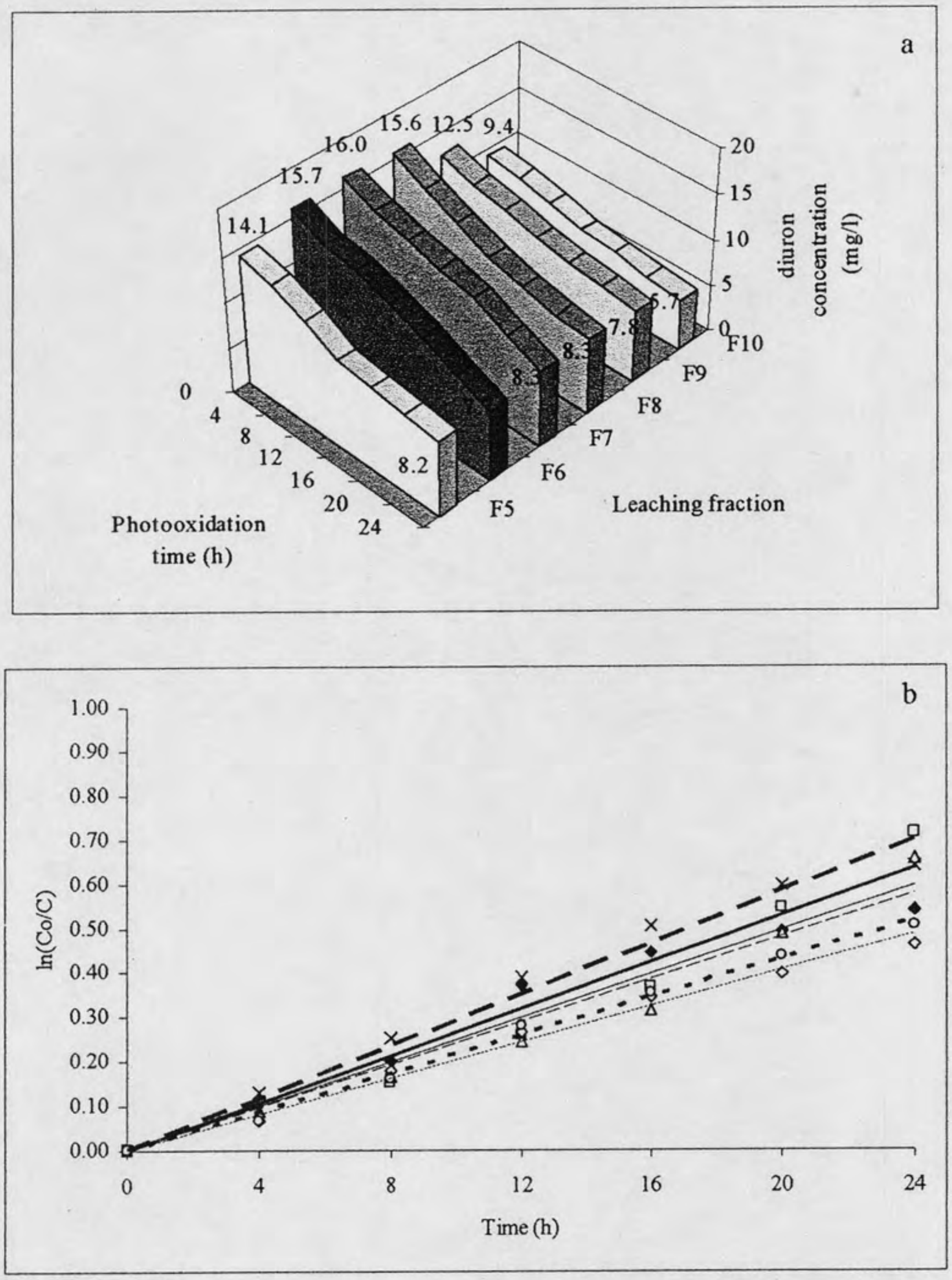


Figure 4.25 a) Photocatalytic degradation of diuron80 vs time of the final fraction (F5) that pretreated with calcium chloride solution and five fractions of leachate (F6-F10) using 10% (v/v) methanol b) First-order linear transforms of the degradation of diuron80: (—◆—) F5, (—□—) (--△--) (– X –) (--◇--) (...○...) refer to F6-F10, respectively.

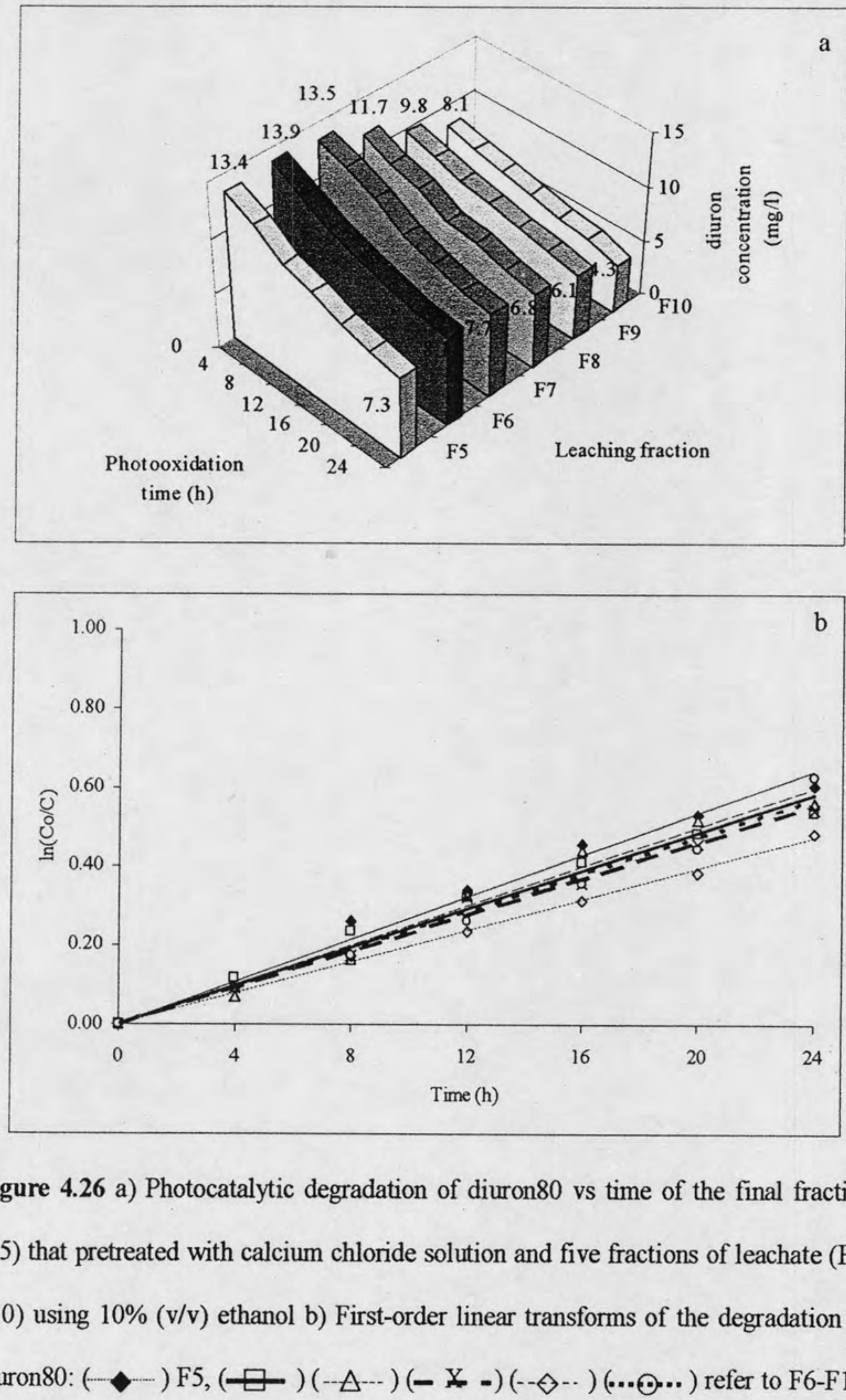
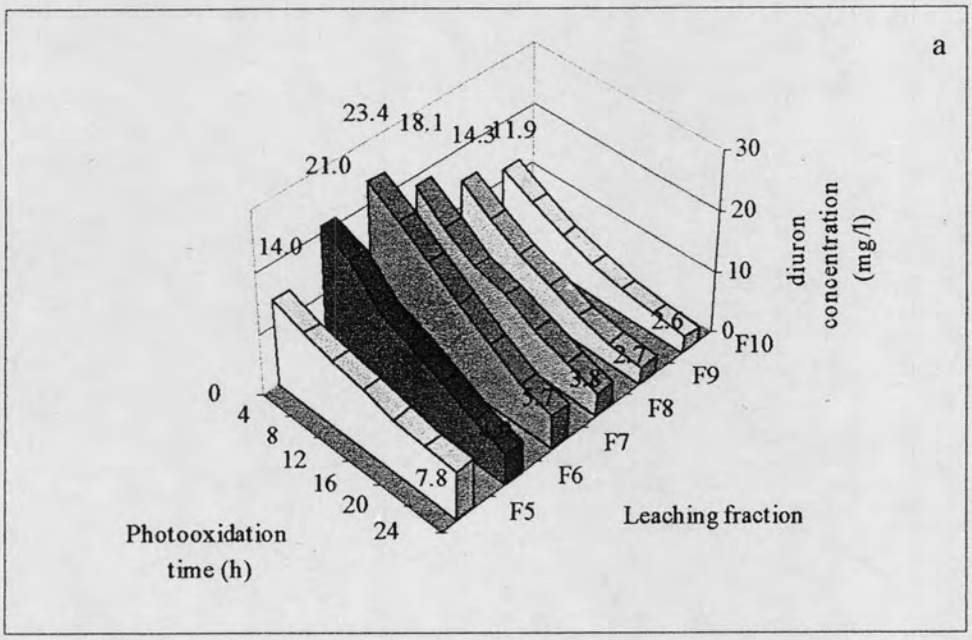


Figure 4.26 a) Photocatalytic degradation of diuron80 vs time of the final fraction (F5) that pretreated with calcium chloride solution and five fractions of leachate (F6-F10) using 10% (v/v) ethanol b) First-order linear transforms of the degradation of diuron80: (—◆—) F5, (—□—) (--△--) (— ✕ –) (--◇--) (•••○•••) refer to F6-F10, respectively.



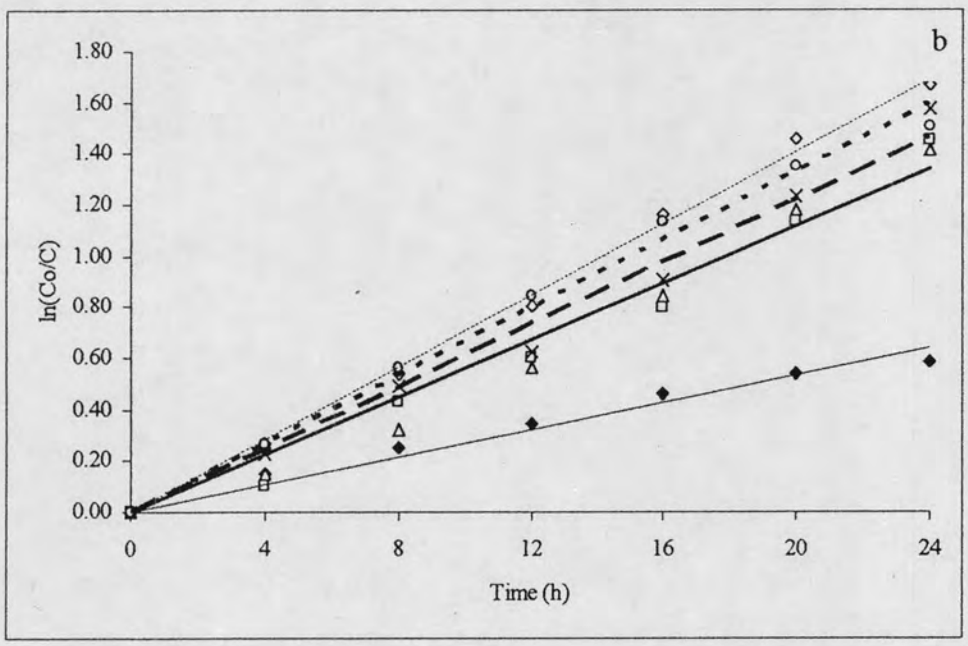


Figure 4.27 a) Photocatalytic degradation of diuron80 vs time of the final fraction (F5) that pretreated with calcium chloride solution and five fractions of leachate (F6-F10) using 10% (v/v) *n*-butanol b) First-order linear transforms of the degradation of diuron80: (—◆—) F5, (—⊟—) (--△--) (— ✕ -) (--◇--) (···⊙···) refer to F6-F10, respectively.

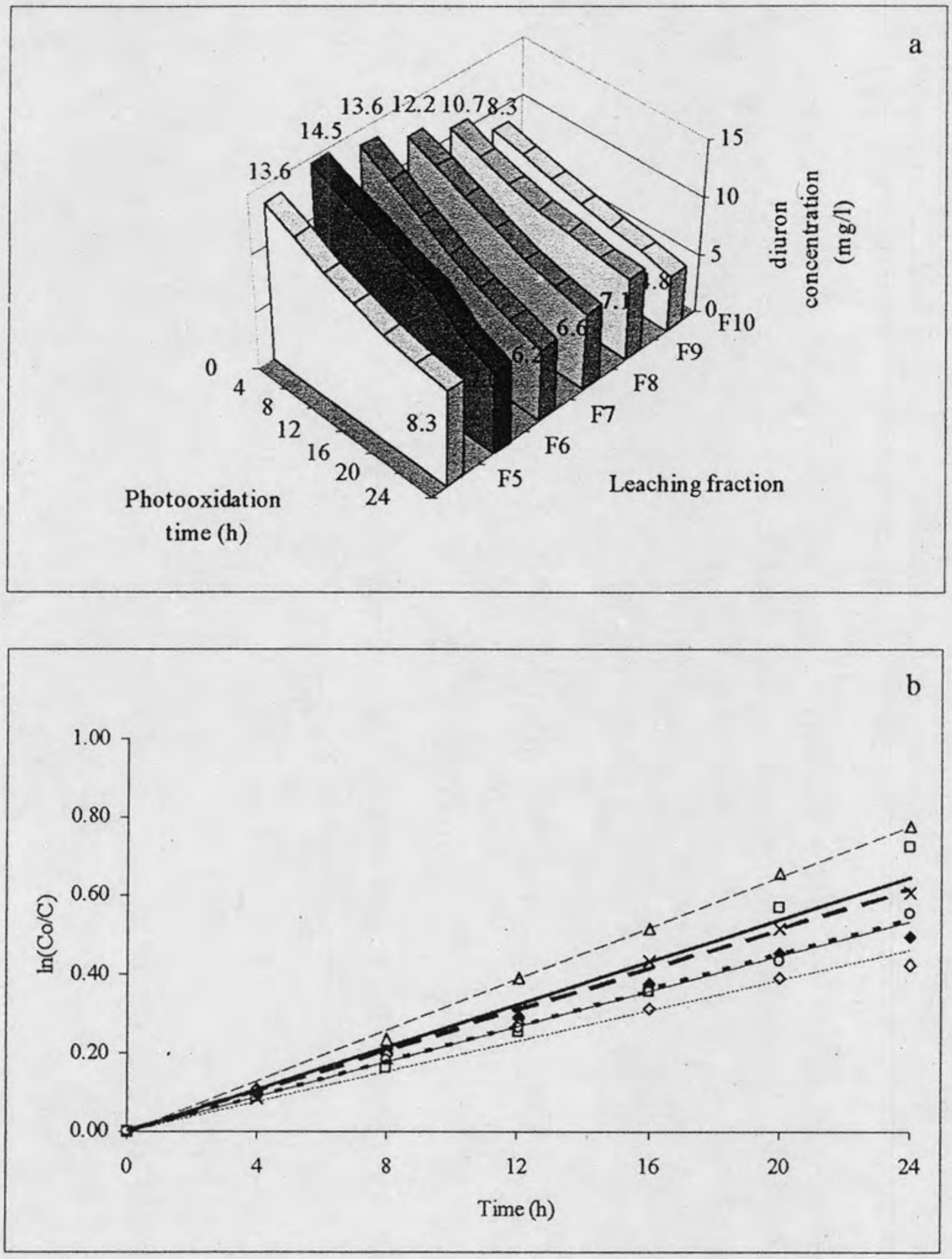
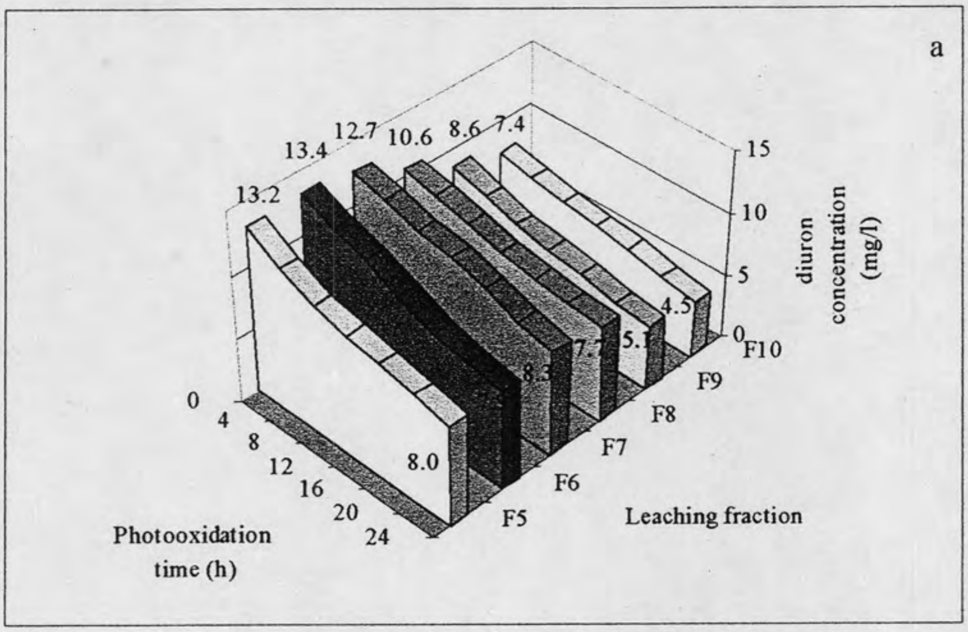


Figure 4.28 a) Photocatalytic degradation of diuron80 vs time of the final fraction (F5) that pretreated with calcium chloride solution and five fractions of leachate (F6-F10) using 20 CMC Triton X-100 b) First-order linear transforms of the degradation of diuron80: (---◆---) F5, (—□—) (--△--) (— X —) (--◇--) (...○...) refer to F6-F10, respectively.



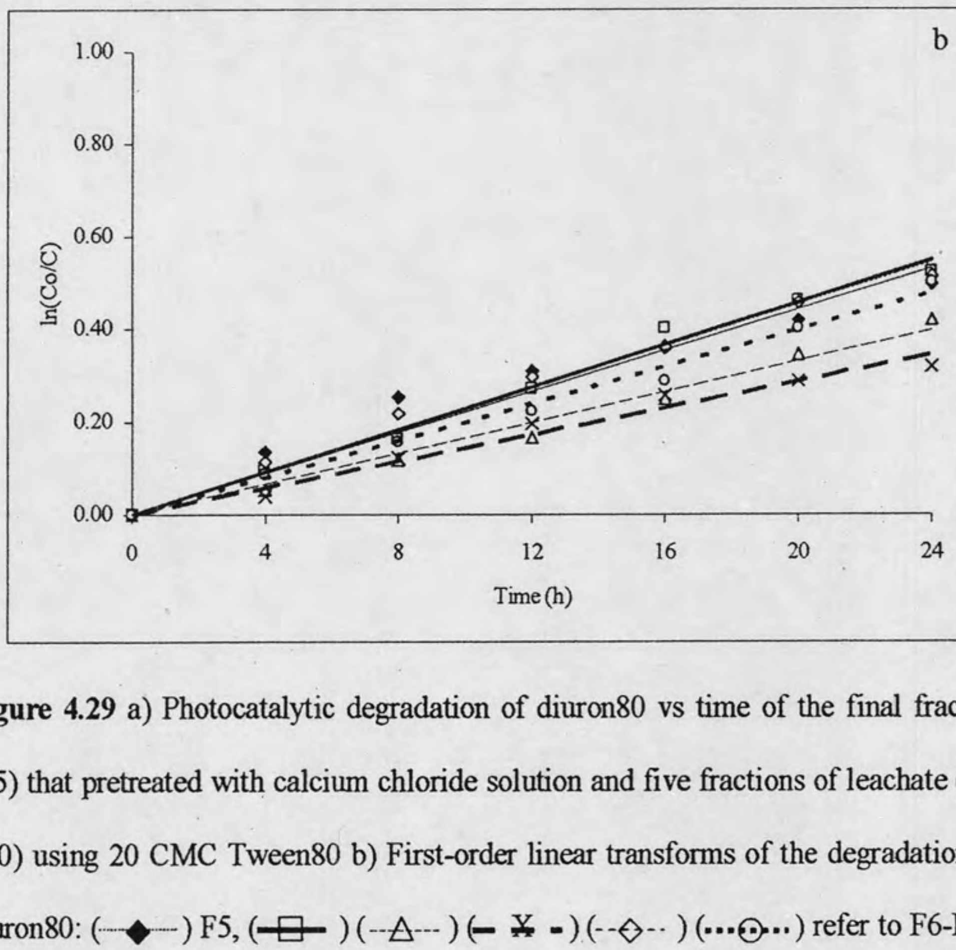


Figure 4.29 a) Photocatalytic degradation of diuron80 vs time of the final fraction (F5) that pretreated with calcium chloride solution and five fractions of leachate (F6-F10) using 20 CMC Tween80 b) First-order linear transforms of the degradation of diuron80: (—◆—) F5, (—□—) (--△--) (— ✕ —) (--◇--) (···○···) refer to F6-F10, respectively.

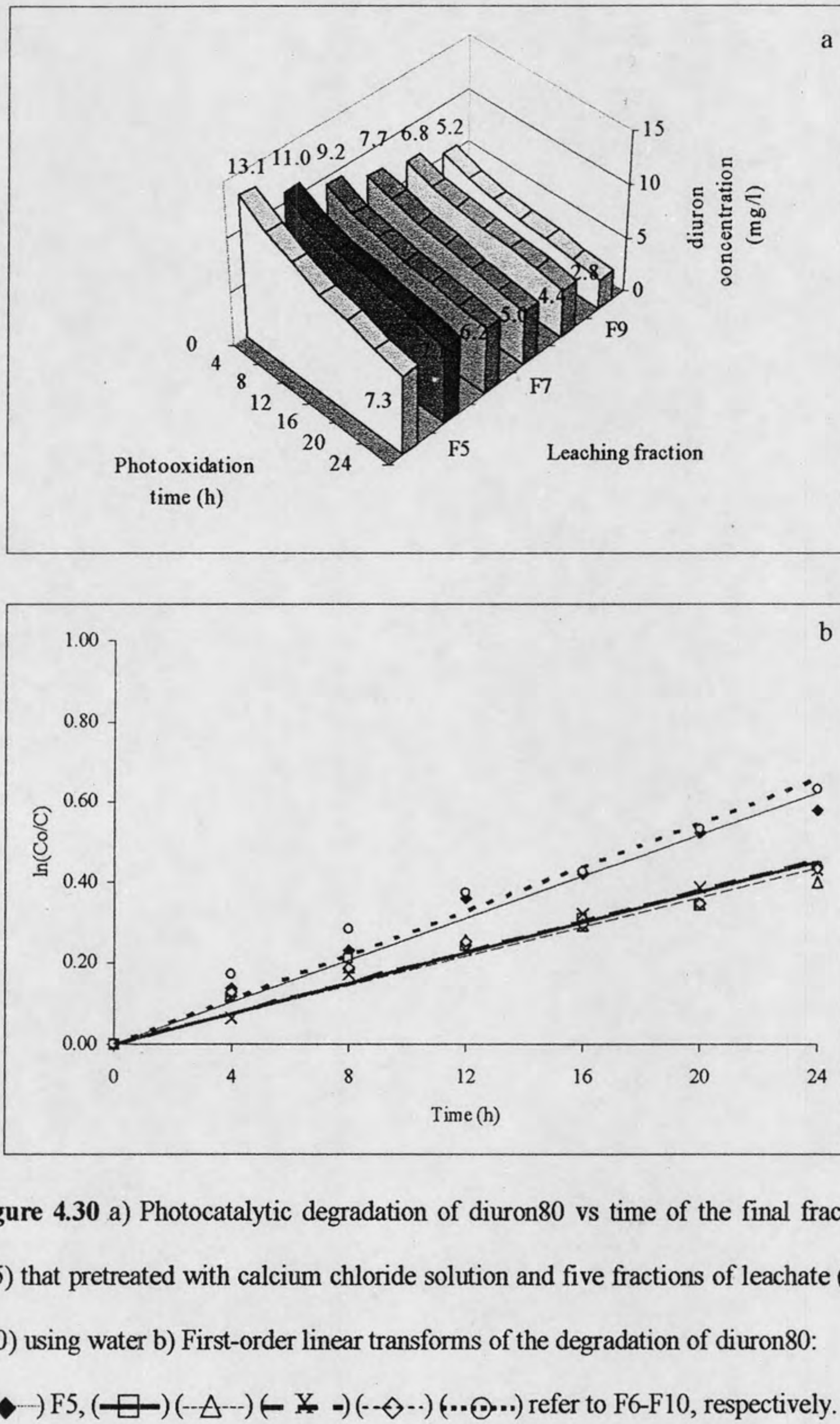


Figure 4.30 a) Photocatalytic degradation of diuron80 vs time of the final fraction (F5) that pretreated with calcium chloride solution and five fractions of leachate (F6-F10) using water b) First-order linear transforms of the degradation of diuron80: (—◆—) F5, (—□—) (--△--) (— X —) (--◇--) (••○••) refer to F6-F10, respectively.

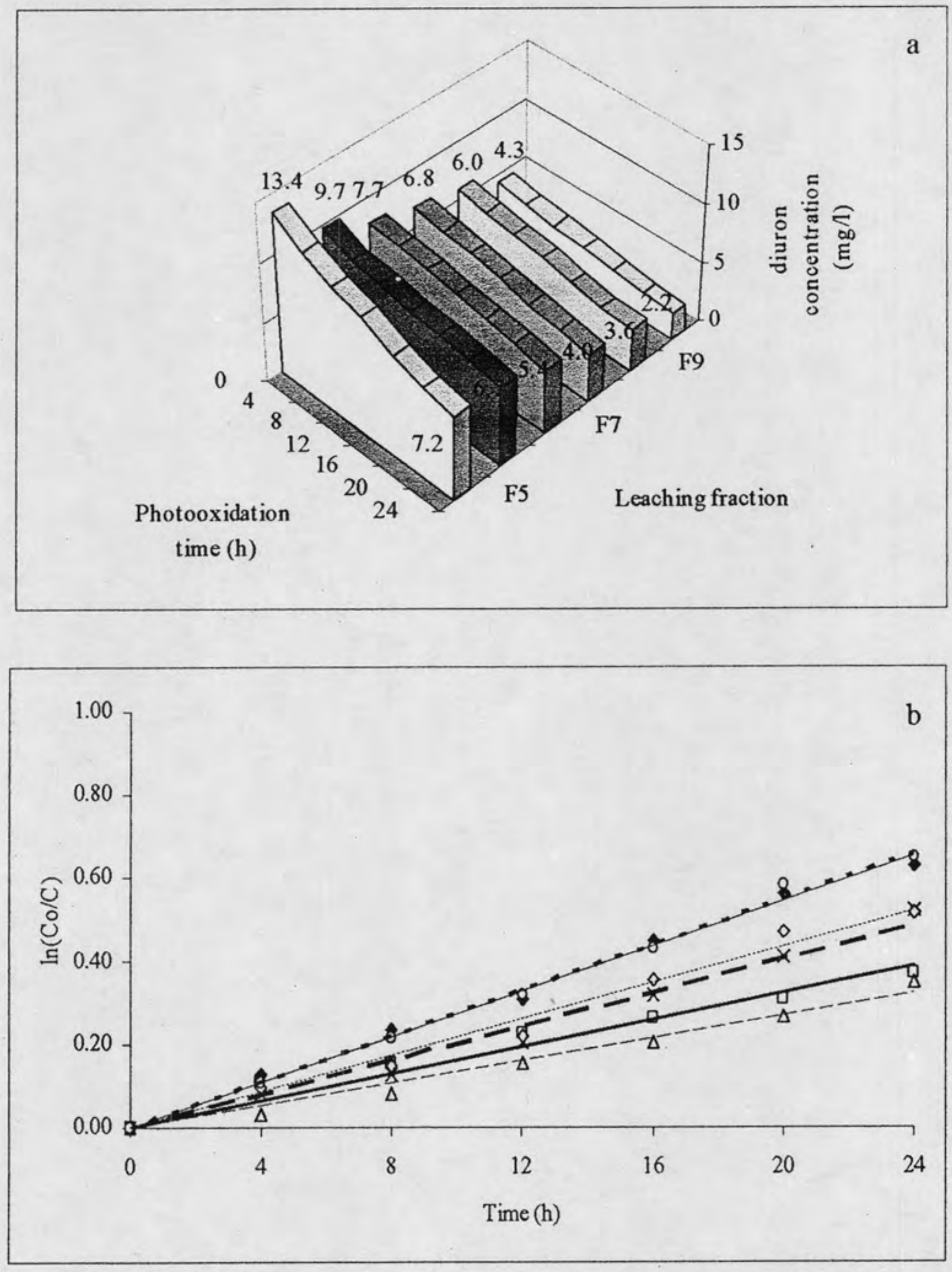


Figure 4.31 a) Photocatalytic degradation of diuron80 vs time of the final fraction (F5) that pretreated with calcium chloride solution and five fractions of leachate (F6-F10) using calcium chloride solution b) First-order linear transforms of the degradation of diuron80: (--◆--) F5, (—□—) (--△--) (— ✕ —) (--◇--) (···○···) refer to F6-F10, respectively.