CHAPTER V

DISCUSSIONS

5.1 Diuron and Diuron80 Solubility

Solubility is one of the most important factors controlling fate and transport of organic contaminants. Where highly soluble materials are quickly distributed, and diluted, insoluble materials are more likely to adsorb on solids, or accumulate in biota. Degradation processes are also concentration-dependent, so insoluble contaminants are more slowly transformed. An estimation of solubility of such compound, therefore, is a crucial first step to modeling fate and behavior. The solubility if diuron and diuron80 was investigated (Table 4.2). The results showed good solubility in short chain alcohol (methanol, ethanol and *n*-butanol), moderate solubility in *sec*-butanol, toluene, benzene and acetone, low solubility in surfactants tested and not soluble in water, *n*-octanol and hexane.

Short chain alcohol is widely used as a solvent. It is relatively safe, and can be used to dissolve many organic compounds which are insoluble in water. The hydroxyl group generally makes the alcohol molecule polar. Those groups can form hydrogen bonds to one another and to other compounds such as diuron. Two opposing solubility trends in alcohols are: the tendency of the polar OH to promote solubility in water, and of the carbon chain to resist it. Thus, methanol, ethanol, and propanol are miscible in water because the hydroxyl group wins out over the short carbon chain. Butanol, with a four-carbon chain, is moderately soluble because of a balance between the two trends. Therefore, higher solubility of diuron in butanol over methanol and ethanol may be effect of hydrophobic carbon chain. The possible reason of different of diuron solubility in *n*-butanol and sec-butanol is steric hindrance. As the length of the alcohol increases, i.e. *n*-octanol, the solubility was decreased, and so the solubility of *n*-octanol falls because the hydrocarbon tail does not form hydrogen bonds. Diuron is soluble in toluene and benzene due to the benzene group on its structure. The reason for the solubility in acetone is that it can hydrogen bond with diuron molecules. There will also, of course, be dispersion forces and dipole-dipole attractions between the acetone and the diuron molecules. Forming these attractions releases energy which helps to supply the energy needed to separate the diuron molecules and acetone molecules from each other before they can mix together. Diuron is quite large compared with a water molecule. In order for diuron to be dissolved, it would have to break lots of existing hydrogen bonds between water molecules. It also has to break the quite strong van der Waals dispersion forces between diuron molecules. Both of these cost energy. The only new forces between the diuron and the water would be van der Waals dispersion forces. These aren't as strong as hydrogen bonds. Diuron is not soluble in hexane, one possible reason is breaking the intermolecular forces within the diuron and hexane costs high energy. The only new attractions between the hexane and diuron molecules are Van der Waals. These do not release enough energy to compensate for what it needs to break the hydrogen bonds in diuron. Therefore, diuron is not dissolved (Clark, 2003).

Diuron is low soluble in surfactant because diuron is not soluble in water while surfactants with hydrophilic-lipophilic balance (HLB) more than 10 (Table 3.2) generally work best with a water-soluble herbicide. Because herbicides and surfactants differ in solubility, it is important to match the solubility of each in order to maximize their performance as a combination (Miller and Westra, 2006).

5.2 Contaminant Adsorption Isotherm

The sorption isotherms of diuron and diuron80 on the soil sample were investigated (Figure 4.1 and 4.4). According to the curves, these isotherms may be generally classified general, as L type of the Giles classification (Giles et al., 1960). The sorption isotherms were compared using the K_f parameter of the Freundlich's adsorption equation (Kipling, 1965). The linear form of this equation is shown in Figure 2.2. The Freundlich isotherm was used to explain the contaminant isotherm using K_f and n value. These values are the constants describing the characteristic of the sorption capacity of the pesticide onto soil of the condition indicated. 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 and 4.4), the Freundlich constant (K_f) is equal to 16.69 $mg.kg^{-1}$ soil and 18.85 $mg.kg^{-1}$ soil for diuron isotherm and diuron80 isotherm, respectively. The slopes (Freundlich exponent, n) of the both diuron and diuron80 isotherms are equal to 1 ($R^2 = 1$). K_f and n are empirical constants characteristic of the contaminant and solid used. In this case, the slope (n) is equal to 1. This means that the affinity of molecules of diuron and diuron80 for the soil remains the same for all level of diuron and diuron80 concentration, respectively (Schwarzenbach et al., 1992). The slopes and K_f parameter of the diuron and the diuron80 isotherm are not significant different, which implies that the adsorption characteristics of diuron and diuron80 are quite similar on this soil sample surface. This result suggests that diuron as well as diuron80 has moderate affinity to the soil used for the treatment and both diuron substances may have high strong competition to the solvent for sorption sites.

In silt clay soils, adsorption of herbicide was mainly by chemical forces (due to high organic matter content) and bioavailability of diuron was less. Hence, the remediation of diuron contaminated soil may be feasible by flushing followed by pump and treat technique (Figure 5.1) (Berglof et al., 2002). Furthermore, van der Waals forces are weak dipolar attractions that occur frequently where non-ionic or non-polar chemicals come into contact with humic acid molecules (Khan, 1995).

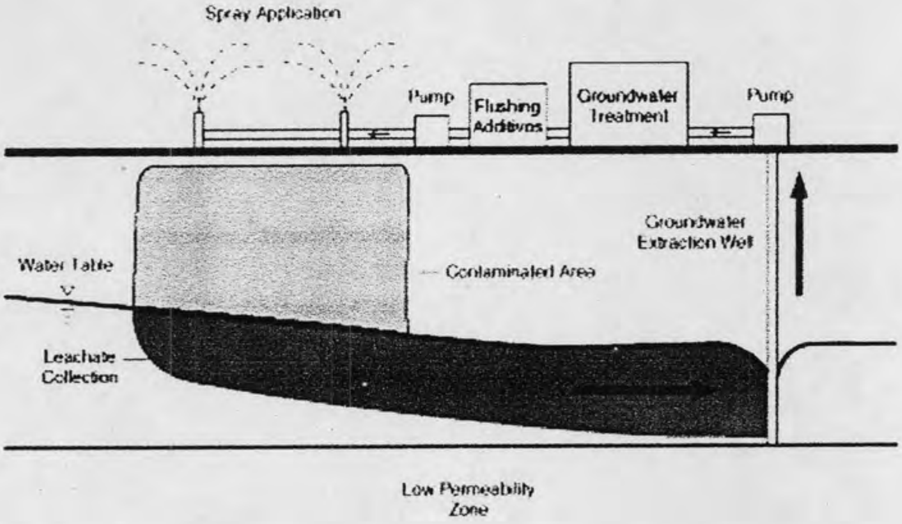

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Figure 5.1 Soil flushing followed by pump and treat technique

In addition, Gonzalez-Pradas et al. (1998) evaluated sorption and mobility of the herbicide diuron in calcareous soil from Spain of varied organic matter content (OC) using peat. Their result showed that it was classified as L type of Giles classification. This result agrees with ours. The K_f values for the soil samples used increase from 2.17 mg.kg^{-1} for the original soil (T-0) (containing 0.18% OC) to 13.12 mg.kg^{-1} and 34.28 mg.kg^{-1} for the T-1 and T-2 samples, containing 1.67% OC and 4.61% OC, respectively. When compare K_f values of our soil (containing 3.93% OC), suggesting that affinity increases as the organic matter content in soil increases. So, if we only consider the lipophilic character of diuron (log $K_{ow} = 2.65$) (Madhun and Freed, 1987), its relatively low water solubility, and the relatively high values of K_{OC}, diuron is not expected to leach a lot in the soils studied; nevertheless soil column studies are also necessary since when organic matter amendment is too high, diuron might bind to the dissolve organic matter, then move through the soil and having possibility to reach and contaminate the groundwater resources (Gonzalez-Pradas et al., 1998).

Walker et al. (2005) studied short-term sorption and demonstrated relative slow sorption of three herbicides (chlorotoluron, isoproturon and triasulfuron) by aggregates of the clay loam soil compared with a sandy loam soil. It was suggested that diffusion of herbicides into and out of aggregates maybe affect availability for leaching in the more structured soil (Walker et al., 2005).

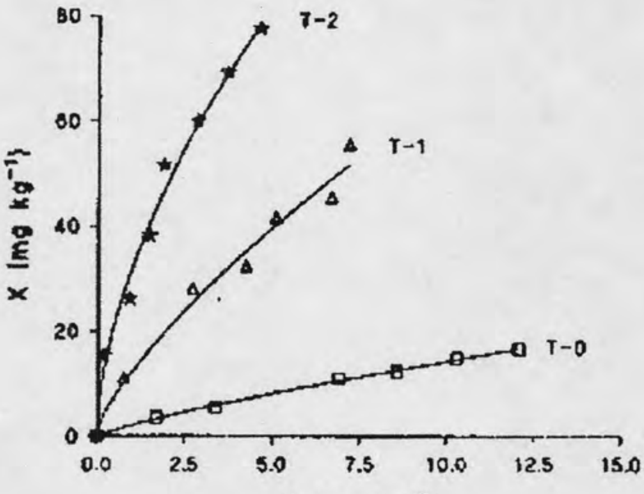

Figure 5.2 Sorption isotherms of diuron on the calcareous soil from Spain. X is milligrams of diuron sorbed per kilogram of soil. C is the equilibrium solution concentration (mg dm^{-3}) (Gonzalez-Pradas et al., 1998).

5.3 Determination of Leaching Conditions of Diuron-contaminated soil

Diuron leaching from soil by water has been widely studied. However, there is little information on the leaching by organic solvent and surfactant. More studies on organic-solvent aided soil washing have been only recently reported. In this study, diuron- and diuron80-contaminated soil washing by organic solvent and surfactant were investigated in soil column condition and under shaking condition to determine a suitable soil washing condition for diuron and diuron80 leaching from contaminated soil.

5.3.1 Determination of leaching conditions of diuron-contaminated soil using soil column and mixing condition (shaking-flask)

(i) *Organic solvent*

Studies of type and concentration of organic solvent on leaching showed that leaching efficiency was increased with increasing short-chain alcohol (methanol, ethanol, *n*-butanol and *sec*-butanol) concentration (1, 5 and 10% v/v). According to the results, alcohols, soluble polar solvents, in water can act well as co-solvent at the concentration ~10% (v/v). Association of co-solvent with hydrophobic organic substances increases the observed solubility and leaching. At lower concentrations, the polar solvent increases solubility slightly by changing the structure of water around the non-polar substance (the co-solute effect). Also low concentrations, the two substances exist in water at their respective solubility limits without interacting (Hermann, 1972).

The results showed that 10% (v/v) *n*-butanol exhibited the highest leaching efficiency in soil column condition (50.99±2.32% w/w and 72.95±1.70% w/w for diuron and diuron80, respectively) and under shaking condition (37.03±0.99% w/w and 48.83±3.34% w/w for diuron and diuron80, respectively). These results related to the highest solubility of the herbicides in *n*-butanol. Since *n*-butanol at 10% (v/v) gave the highest leaching efficiency for both diuron and diuron80 and under both conditions, it was suggested that *n*-butanol was the best organic solvent to be used for soil washing under the conditions indicated.

The investigation of leaching using toluene, benzene and acetone was also carried out. The results show insignificant difference of leaching efficiency using these solvents at concentration 1% (v/v). Use of high concentration of these solvent in soil washing was limited because they have high viscosity and toxicity as described previously in Result 4.4.2. Moreover, persistence problem of toluene and benzene in environment may be occurred because of their low water solubility.

The effect of different isomer type of organic solvent on herbicide solubility was investigated using *n*-butanol and *sec*-butanol. Leaching of diuron by *sec*-butanol resulted in less leaching efficiency when compared to that of its isomer. The possible reason was evident from solubility study that steric hindrance effect of side chain of *sec*-butanol might decrease diuron solubility. Therefore, the compatibility of the herbicide and organic solvent would result in high leaching efficiency.

(ii) *Surfactant*

Effect of type and concentration of surfactant on leaching was investigated. At low concentration (1, 2 and 8 times CMC of surfactants), increasing of nonionic surfactant concentrations, i.e. Triton X-100, Tergitol NP10, Tween80 and Brij35, did not show much effect in enhancing the leaching efficiency of diuron and diuron80. However, leaching efficiency was increased when these chemical surfactant concentrations was increased to 20 times of their CMC. These results could suggest that diuron was dissolved more in the micellar phase at a relative high level of the surfactant concentration. The high CMC value also caused some dispersion of soil colloid in the system. The soil colloid can also sorb diuron, thereby decreasing the enhanced efficiency of diuron from soil to water (Thibault et al., 1996). However, limited of soil washing using surfactant have been performed over a long period of time. Some of the limitations may include low soil permeability, heterogeneity and extreamly insolubility of the contaminants (Mulligan et al., 2001).

Leaching efficiency using anionic surfactant SDS showed higher efficiency than those of other nonionic surfactants at low concentration (1 and 2 CMC) because SDS could disperse soil particles, therefore, diuron-sorbed dissolve organic matter was leached. However, because of the obstruction of liquid flow in the column at high CMC value of SDS and the precipitation of dodecyl sulphate to the soil phase as described by Jafvert (Jafvert, 1991), SDS are not suitable to use as an exclusive soil-washing agent in this study.

The results showed that 20 CMC TritonX-100, a nonionic surfactant, has highest leaching efficiency in soil column condition (39.68±2.73% w/w and 45.07±1.19% w/w for diuron and diuron80, respectively) and under shaking condition (25.55±2.00% w/w and 40.39±2.97% w/w for diuron and diuron80, respectively) when compared to those of other surfactants used in the experiment. Triton X-100 was also previously reported to be the most suitable surfactant for soil leaching for PAHs 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). Therefore, in this study Triton X-100 was the best surfactant for leaching from soil over other surfactant tested. However, diuron leaching from the soil tested using 20 CMC Triton X-100 showed less efficiency than that when 10% (v/v) *n*-butanol was used.

Hartley and Graham-Bryce (Hartley and Graham-Bryce, 1980) showed that an increase in solubilization in water of nonpolar organic chemicals is obtained when surfactants are present in the water solution. However, the solvent power of surfactants is much greater than that of a simple cosolvent. The total solvent power is determined by the number of micelles, their size and structure, and is not proportional to surfactant concentration. The limitation comes from the fact that the micelle cannot increase indefinitely in size without modifications of its structure and properties due to reorientation of surfactant molecules.

As for the results of static and mixing 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.

(iii) *Type of herbicide*

Effect of type of herbicide on leaching showed that leaching efficiency using organic solvent and surfactant tested towards commercial-grade diuron80 from soil was higher than that of diuron suggesting that it was comparatively loosely bound to soil. In a general sense, pesticide formulations contain besides the active ingredients many other compounds, i.e. adjuvants. Adjuvants are chemicals added to enhance the effectiveness (bioavailability) of the pesticide formulation by enhancing the solubility, or the compatibility of the active ingredients (Krogh et al., 2003). Therefore, commercial grade herbicides having adjuvants exhibited more water solubility, thus having the greater the likelihood for leaching compared to the analytical grade, containing more active ingredient.

Effect of water solubility of the organic compound on leaching was reported by Landry et al. (Landry et al., 2005), who studied the leaching of diuron and oryzalin through undisturbed soil columns using three vineyard soils: a rendosol, a calcosol and a vegetated calcosol. A greater proportion of soil leaching residues was obtained for diuron (3.2%, 11.8% and 18.8% of applied diuron, respectively) than for oryzalin

(0.2%, 4.9% and 3.7%, respectively). The greater mobility of diuron was related to its higher water solubility (36.4 $mg.l^{-1}$ compared with 2.6 $mg.l^{-1}$ for oryzalin) and to its smaller adsorption coefficient (400 $l.kg^{-1}$, compared with 700-1000 $l.kg^{-1}$).

(iv) *Aging of the diuron in soil*

Effect of contaminant aging on leaching was carried out in two conditions, i.e. 1-week (short-term) and 1-month (long-term) aging of either diuron and diuron80 in the soil sample. The 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 5.1 and 5.2 was resummarized from results of Table 4.3-4.8 that show leaching efficiency of 1-week diuron and diuron80 aged soil was higher than 1-month diuron and diuron80 aged soil, suggesting that aging of contaminated residues in soil leaded to increase of contaminant sorption and reduced availability of contaminant for leaching. Therefore, long-term contamination of diuron may cause a stronger sorption onto soil becoming less extractable and less bioavailable. Further, the sorption irreversibility increased with increasing soil-pesticide contact time. Such phenomena have been observed for numereous non-ionic organic compounds and are related to physical sequestering processes (Pignatello and Xing, 1996). These results therefore indicated that time-dependent sorption processes are important in controlling pesticide movement in soils, although the data do not give a mechanistic explanation of the changes in leaching with aging of residues.

Similar phenomena was reported by Walker et al. (Walker et al., 2005), who investigated influence of aging of residues on the availability of three herbicides (chlorotoluron, isoproturon and triasulfuron) for leaching. The results from small scale leaching studied with aggregates of the soils also demonstrated reductions in availability for leaching as residence time in soil was increased, which could not be explained by degradation. These results therefore indicate that aging of residues leads to increased sorption and reduced availability for leaching.

Rodriguez et al. (Rodriguez-Cruz et al., 2006) reported that desorption rates of herbicides, atrazine and linuron, from sandy loam soil (7.28% OC) decreased with the increase in the aging time. Their results also showed that amount of herbicide was desorbed 10-fold and 9-fold higher than that desorbed in water when 10-CMC SDS and 100 CMC Triton X-100 were used, respectively. They also suggested the use of surfactants for increasing the desorption of atrazine and linuron from soils polluted with these compounds after a long aging time in the soil.

(v) *Leaching condition*

Leaching of diuron- or diuron80-contaminated soil was investigated in two conditions at room temperature: static condition (soil column) and mixing condition (shaking-flask). Soil column condition is necessary to study movement, sorption and leaching of contaminant for *in situ* soil washing, while shaking-flask condition is studied for *ex situ* soil washing in mixing tank. Interestingly, leaching efficiency of the herbicides from soil in soil column was higher than under shaking condition. The description of this phenomenon might be the effect of soil moisture. In fact, contact area of soil (soil surface area = 30.12 $m^2 g^{-1}$) with solvent under shaking condition is higher than that in static condition. In this case, Calvet (Calvet, 1989) suggested that pesticide are usually transported to the adsorbing surfaces by water. The moisture content determines the accessibility of the adsorption sites, and water affects the surface properties of the adsorbent. Studies of pesticide-clay-water systems have been remarkably useful for archiving an understanding of the effect of water on pesticide adsorption (Green, 1974; Burchill and Hayes, 1981). Absorbed water provides adsorption sites for pesticide molecules. An important feature of water associated with clay surfaces is that it increases ionic dissociation of clay surface, giving the surfaces a slightly acidic character. Generally, a negative relationship exists between the surface acidity of clays and their water content. The studies of the effect of hydration of the soil organic matter in relation to pesticide adsorption has been suggested that hydration influences the molecular shape of humic substances, and thus accessibility for pesticides. The strong, irreversible retention of pesticides by hydrated humic substances could be explained by the penetration and trapping of pesticides into the internal structure of the swollen humic substances (Burchill and Hayes, 1981). Therefore, diuron may exhibit stronger sorption in soil under shaking condition.

Another possibility of this phenomenon is that the first reactions between foreign chemicals and soil are physically-chemically reversible interactions (Lehmann *et al.*, 1990; Barriuso *et al.*, 1992). Therefore, leached diuron in solvent under shaking condition may be higher reversed to soil because longer contact time between soil and solvent than that in soil column condition.

Table 5.1 Leaching of diuron- and diuron80-aged soil packed in soil column for 1 week and 1 month using organic solvent and surfactant.

Organic solvent and surfactant	Leaching of diuron from soil			
	Diuron (% w/w)		Diuron80 (% w/w)	
	1 week	1 month	1 week	1 month
Methanol (1% v/v)	35.38±2.38	32.13±1.81	49.97±4.20	36.51±4.22
n-Butanol (1% v/v)	45.83±3.41	40.49±3.32	54.31±2.24	47.56±4.09
Toluene (1% v/v)	30.36±2.56	29.95±0.89	45.44±2.54	36.03±2.27
Triton X-100 (2 CMC)	32.80±1.69	32.29±1.85	39.62±1.52	35.34±1.87
SDS (2 CMC)	36.83±0.55	30.20±1.48	44.02±3.54	41.85±4.01

Water	33.03±1.55	27.12±2.37	46.31±3.91	28.87±1.38
0.01 M $CaCl_2$	32.48±1.51	27.05±2.76	45.32±1.33	30.38±0.68

Table 5.2 Leaching of diuron- and diuron80-aged soil under shaking condition for 1 week and 1 month using organic solvent and surfactant.

Organic solvent and surfactant	Leaching of diuron from soil			
	Diuron (% w/w)		Diuron80 (% w/w)	
	1 week	1 month	1 week	1 month
Methanol (1% v/v)	28.52±2.67	17.03±2.55	38.11±2.16	30.82±3.93
n-Butanol (1% v/v)	29.48±1.36	17.03±2.54	42.46±3.32	48.83±3.34
Toluene (1% v/v)	29.31±1.78	26.41±1.12	41.35±3.50	34.86±4.13
Triton X-100 (2 CMC)	26.20±1.67	17.71±0.32	41.07±2.57	34.05±4.27
SDS (2 CMC)	30.99±1.45	28.11±0.94	44.85±4.07	39.28±5.71
Water	17.14±2.55	11.82±1.34	32.65±0.78	23.59±3.49
0.01 M $CaCl_2$	18.73±1.45	11.91±1.79	33.11±2.75	24.09±2.20

5.3.2 Effect of combination of suitable organic solvent and surfactant

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. One conclusion which can be drawn from the investigations is that the combination of proper solvent (*n*-butanol in this case) and a surfactant solution (Triton X-100, in this case) enable a much higher soil-washing capability in the leaching of diuron from silty clay soil. This mechanism likely originates from the special structure of the micellar core of surfactants. The surfactant micelle formation becomes appreciable at the CMC. The micellar core is a liquid-like hydrocarbon interior acting as an organic pseudophase into which hydrophobic contaminants are partitioned. The addition of a solvent efficiently assists the dissolution of hydrophobic contaminants into the aqueous phase from the soil particle, due to the much smaller size of the solvent molecules than that of surfactant micelles. After the contaminants are transferred from the soil phase to the liquid phase, they can either be kept in the liquid phase or be captured by the micellar core, and both cases are considered valid decontamination (Chu and Kwan, 2002).

In addition, the solvent itself may also be solubilized into the core, resulting in a solvent-incorporated surfactant micelle. The dissolving of a solvent into micelles may enlarge the effective core size and advance the hydrophobic contaminant partitioning capacity of the micelles as its non-polar organic content is increased. The organic pollutant will have a higher affinity to partition into a micellar core where the solvent molecules are resident. Therefore, the overall extraction performance using a surfactant/solvent solution is much better than the original surfactant-aided soil-washing process, and especially useful for the remediation of contaminated soil that has been polluted by hydrophobic compounds. However, if the polarity of the solvent is too low, the surfactant may become a bridge to link the solvent, pollutant, air, and water molecules together, resulting in a stable and inseparable emulsion and therefore failure of the soil-washing process (Chu and Kwan, 2003).

Moreover, the results showed insignificant increasing of leaching efficiency when the concentration of Triton X-100 was increased. The saturation of surfactant micelles might be the reason for this phenomenon. After the micellar cores were saturated by contaminants and solvent, the extraction function of the surfactant ceased and the extraction capability resulting from the surfactant micelles could be considered as a constant (Cheng et al., 2001).

The modified surfactant-aided soil-washing system which involves adding organic solvent to the system has been proven useful in promoting overall soil-washing performances as reported by Chu and Kwan (Chu and Kwan, 2003), who found that the acetone/surfactant systems can improve the overall extraction of 4,4'-dichlorobiphenyl (DCB) out of soil by 15-25% w/w compared to that when surfactant was used alone (in which the ratio of acetone/surfactant is zero). They suggested the micellar-solubilized solvent has a positive effect in promoting the partition process and increasing the driving force for removing hydrophobic contaminants.

5.3.3 Effect of pH on leaching of diuron in soil

An attempt was made to investigate the effect of pH on diuron leaching process. The soil was pre-equilibrated to pH 6 and 8 before the leaching. Changing of soil pH does not change the ionic characteristic of the nonionic-herbicide diuron but it changed soil properties and affect the adsorption of the herbicide.

Leaching of diuron by 10% (v/v) *n*-butanol and 20 CMC Triton X-100 at lower pH (pH6) showed that the soil leaching of diuron and diuron80 decreased. Diuron leaching efficiency from soil at pH 6 less than these at pH 7 and pH 8 with approximated 3-9% w/w and 4-6% w/w, and, for diuron80, 2-5% w/w and 7-9% w/w, respectively. The difference on leaching efficiency may be due to the fact that the higher pH caused more soil organic matter to dissolve in solution and more acidic groups to dissociate. Dissociation of acidic groups would result in soil organic matter to be more hydrophilic, increasing diuron leaching (Liu et al., 1995).

Therefore, the insignificant effect of pH was expected because the London forces between diuron molecules and the electrically neutral portions of soil surface in this condition do not change with pH (Sheng et al., 2005). However, in our study, pH change might have affected the clay mineralogy or destructed the crystal lattice. This may be the reason for high leaching of adsorbed diuron (Kumar and Philip, 2006).

In the earlier studies, Sheng et al. (Sheng et al., 2005) investigated pesticide (diuron) sorption in soil containing crop residue-derived chars and evaluated the influence of soil pH on pesticide sorption in soils containing chars. Figure 5.3 shows one of their results, i.e. the isotherms of diuron sorption from water by soil, wheat char, and char-amended soil at two pHs. The sorption of diuron on the soil at pH 6.0 was slightly lower than that at pH 3.0. The sorption difference may be due to the fact that higher pH caused more soil organic matter to dissolve in solution and more acidic groups to dissociate. Dissociation of acidic groups would result in soil organic matter to be more hydrophilic, reducing diuron sorption. As a neutral molecule, the sorption of diuron in the presence of wheat char was primarily controlled by the char and not influenced by pH. The isotherms with wheat char conformed the Langmuir-type, suggesting the influence of surface adsorption, a mechanism primarily responsible for sorption by activated carbon. The lack of a pH effect further suggested that diuron was sorbed on the carbon fraction of wheat char. Sorption of diuron by char-amended soil was enhanced, as compared to char-free soil, confirming earlier prediction that the presence of chars (organic matter) in soil enhances the pesticide sorption by the soil. As shown with wheat char, no pH effect was observed with charamended soil, apparently because of the predominance of the char in sorbing diuron.

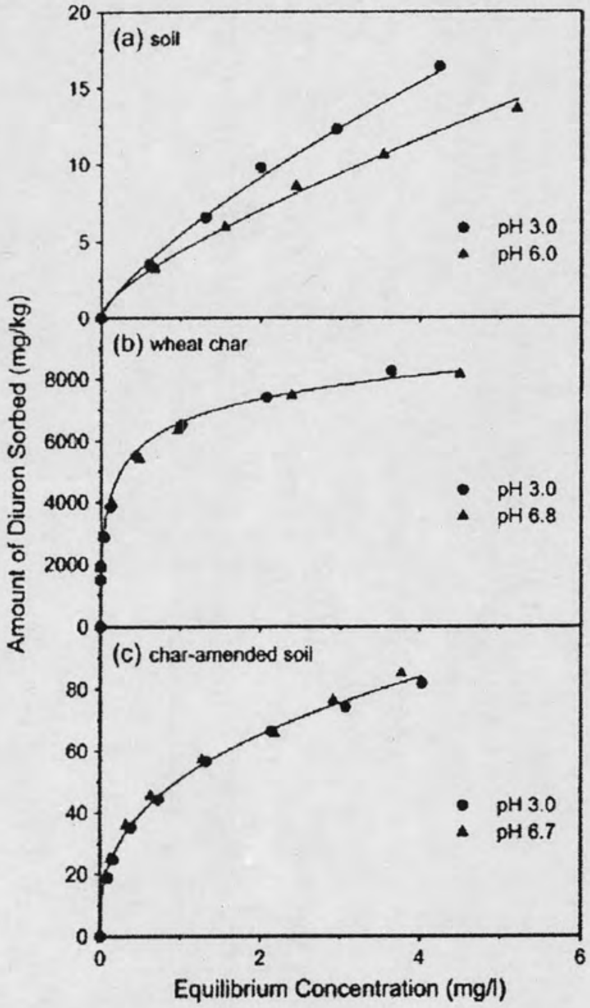

Figure 5.3 Isotherms for sorption of diuron from water by soil, wheat char, and 1% char-amended soil as in fluenced by pH (Sheng et al., 2005).

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

Ionic strength and the dominant cationic markedly have been reported to influence the leaching of diuron. The results show that 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 decrease in leaching efficiency was found to be in the range of 5-16% w/w for diuron and 3-8% w/w for diuron80. An increasing in the ionic strength of the system (0.03, 0.15 and 0.3 M using calcium chloride solution) leaded to replacement of protons from soil surface and caused a slight pH decrease. Sorption of the neutral species can be altered by the effects of ionic strength (μ) on aqueous activity, which is observed as the "salting out" effect on the hydrophobic partitioning. The conceptual model for this relates to the strong tendency of ionic solutes to form shells of tightly-bound water (hydration shells). As the concentration of ions increases, more and more water is bound up in hydration shells, and less "free" water is available for forming cavities and icebergs around the organic solute. This process is called electrostriction. Different type of salts have different abilities to coordinate water (Setschenow, 1889). This effect can be varied directly or inversely with salt concentration, and depending on the salts (e.g., NaCl, $CaCl_2$, and KCl), although generally an increase in sorption occurs with increasing salt concentrations (Lee et al., 1990). In our results, soils with high Ca^{2+} (high ionic strength) may react with herbicide to form water insoluble calcium salts and decrease leaching. For hydrophobic compounds, such as PAHs (i.e., benzo[a]pyrene), the ionic strength of the aqueous phase had a strong effect on desorption from soil (Kogel-Knabner et al., 2000) presumably due to the effects of ionic strength on aqueous activity (Chiou and Schmedding, 1982).

In our investigation; however, the effect of ionic strength was insignificant in the leaching of diuron and diuron80 using 20 CMC Triton X-100. The possible reason for this phenomenon could be that the change in CMC for non-ionic surfactants attributed to "salting in" or "salting out" effects. If energy required was increased by electrolyte, activity coefficient of solute was increased and salting out occur, micellization is favored and CMC decreases. Therefore, leaching efficiency of Triton X-100 was increased from salting out effect (Miyagishi et al., 2001). This result contradicts a study by Alva and Singh (Alva and Singh, 1991), who observed an increase of the sorption coefficients of four herbicides (bromacil, diuron, norflurazon, and simazine) with increasing ionic strength.

Interestingly, leaching of diuron and diuron80 using 20-CMC Triton X-100 was not strongly affected by ionic strength, but was influenced by pH. The similar result was stated by de Jonge and de Jonge (de Jonge and de Jonge, 1999), who observed adsorption and desorption parameters for non-ionic fungicide prochloraz. They founded the effect of ionic strength in the pH-neutral treatments was too small to measure significant changes on the sorption bulk soil (K_f = 57.5-78.2), but it was influenced by pH and the presense of ortho-phosphate (K_f = 30.4-152). The pH-rise after addition of NH_4OH and $Na_4P_2O_7$ reduced the adsorption coefficient by nearly 50%. As prochloraz is a neutral compound, the solution chemistry does not directedly influence the sorption mechanism. Rather, dissolve organic matter was solubilized at the high pH levels and complexed with prochloraz, leading to a reduction in the measured sorption coefficient.

5.4 Photodegradation of Diuron

The chemical structure of diuron, which is one of the complicated-structure man-made compounds, includes a benzene ring, two chloride atoms and an alkylurea group as shown in Figure 1.1. To degrade or remedy its contamination in the environment, chemical and biological processes can be applied. In this study, the photocatalytic degradation of diuron using titania as catalyst was investigated.

To apply photodegradation to the contaminated pesticide in the environment, it has been reported that the rate of direct photolysis of pesticide on soil surfaces are much slower than that of the pesticide soluble in water because of the light-attenuating effect. Therefore, in this study, we firstly leached diuron contaminating in soil using aqueous solution of 10% (v/v) organic solvent (methanol, ethanol and *n*-butanol) or 20 CMC surfactant (Triton X-100 and Tween80) or control solvent (water and calcium chloride solution). Diuron dissolved in the solution was then further treated the leached diuron using the photolysis process.

In a previous report, Klongdee et al. (Klongdee et al., 2005) showed that titania synthesized by thermal decomposition method had higher photocatalytic activity for the degradation of 1 ppm diuron solution than the reference catalyst (JRC-TI0-1). It was suggested that the higher rate and diuron degradation efficiency in those conditions were the results of high crystallinity of synthesized powder, which consequently reduces the recombination of photogenerated electron-hole pairs. The degradation of diuron achieved by the synthesized titania was in the range of 70-80% within 6 h of reaction, using standard UV lamp. Therefore, titania synthesized by this method was employed as catalyst in the photodegradation of diuron in this work, due to high activity in photocatalytic decomposition.

In our results, 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 of both diuron and diuron80, comparing to other solvent. R-squared values of the first-order kinetics fitting approached 1, which indicates that the photooxidation on titania was in agreement with the Langmuir-Hinshelwood model. However, the total disappearance of diuron was not achieved even after 24 h. These results seem surprising since it is well-known that in water system (Figure 4.23 and 4.30), $^{\bullet}$OH are formed and these radicals are very efficient in promoting various degradation process. The same trend was observed by Bouquet-Somrani et al. (Bouquet-Somrani et al., 2000), who reported that diuron degradation is faster in acetonitrile (CH_3CN) than in semi-aqueous system (CH_3CN-H_2O, 2.6:1 by volume). After 8 h of irradiation in acetonitrile, the disappearance of diuron was complete, whereas in acetonitrile-water, the degradation of diuron was not complete after 24h.

Interestingly, the highest rate of photocatalytic degradation was found in fractions leached from soil column using 10% (v/v) *n*-butanol solution, although the fractions contained the highest initial concentration of diuron, comparing to other solvents. The possibility of the phenomenon is that the humic materials, i.e. a complex mixture of polymeric phenolic macromolecules, can also be extracted from soil by soil—washing process. These materials also have the ability of photosensitization to absorb solar energy and generate radical species that may attack chemicals in the environment and initiate their degradation (Zepp et al., 1981). Humic acids (HA) are the fraction of humic substances that is not soluble in water under acidic conditions (pH < 2) but is soluble at higher pH values. They can be extracted from soil by various reagents. As humic acids contain free and bound phenolic OH-group structures, nitrogen, and oxygen as well as several COOH groups on aromatic rings, they are the major extractable component of soil (Steveson, 1982). Therefore, humic acid may be leached from soil by 10% (v/v) *n*-butanol in higher amount than other system, resulting in an enhancement in the photodecay of diuron. This is supported by the study by Chan and Chu (Chan and Chu, 2005), who observed that humic acid, which was co-extracted from the surfactant-aided soil-washing system, was capable to improve the photolysis of atrazine at low concentration, while quenching the photodegradation of atrazine at higher concentration. In addition, HA has been shown to facilitate TiO_2/UV oxidation process (Schmelling et al., 1997). Besides being a scavenger of radicals, HA may act as a light filter and consume most of the photon during the photolysis process (Hawari et al., 1992).

This contradicts a study by Klongdee et al. (Klongdee et al., 2005), who demonstrated that the degradation rate of diuron with high initial diuron concentration (C_o = 10 ppm) was only slightly less than that of low initial diuron concentration (C_o = 1 ppm).

The photodegradation of pesticides can be expressed as follows:

$TiO_2 + h\nu \rightarrow e^- + h^+$ (1)

$(O_2)_{ads.} + e^- \rightarrow (O_2^{\bullet -})_{ads.}$ (2)

$Ti(IV) - OH + h^+ \rightarrow Ti(IV) - OH^{\bullet}$ (3)

$Ti(IV) - H_2O + h^+ \rightarrow Ti(IV) - OH^{\bullet} + H^+$ (4)

$\text{compound} + h^+ \rightarrow \text{compound}_{\text{oxidized}}$ (5)

The resulting $OH^{\bullet}$ radical, being a very strong oxidizing agent (standard redox potential + 2.8V) can oxidize most of organic pesticides to the mineral end products (Herrmann, 1999). This suggests that the exact mechanism is influenced by several factors including the organic substrates (initial and intermediates), depending on their nature and on the experimental conditions.