

## CHAPTER II

### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Literature Review

Early laboratory studies of soil washing using batch extraction and column studies were deemed successful. Moreover, the studies of diuron leaching and degradation by photooxidation have been published. Some of those works are discussed as below

Ellis and coworker (1985) described the use of an aqueous solution of nonionic surfactants for flushing PCBs, petroleum hydrocarbons and chlorinated phenols from soil. Results of column experiments showed that the initial wash had little effect. However, with surfactant washing, 74.5% of the pollutant was removed after the third pore volume. Additional surfactant increased the removal to 94% after ten pore volume. The pollutant concentration on the soil was reduced to 6% of the initial spike value after washing with ten pore volumes of surfactant. The final water rinse also showed only minimal effect. It can be concluded that the surfactant can be used to remove those organic contaminants effectively, with an order of the magnitude greater than those obtained by flushing with water alone (Ellis et al., 1985).

Peters and coworker (1992) used surfactant solutions, for example Triton X-100, Brij35, Ethylan GE08, Ethylan CD127, and Ethylan CPG660, to leach undistributed soil cores taken from a site that had been contaminated with No.2 diesel fuel after a puncture of a transfer line. Preliminary screening of 22 surfactants was performed prior to this study to choose surfactants to be used in the flooding of the

Gonzalez-Pradas and coworker (1998) evaluated the behavior of the herbicide diuron in peat-amended calcareous soil from Spain. They studied the sorption and leaching of diuron from 0.02 M CaCl<sub>2</sub> aqueous solution at 25 °C from soil after organic carbon (OC) amendment with a commercial peat (from 0.18% to 4.61%) by using batch and soil column experiments. The experimental sorption isotherms were classified as L type of the Giles classification. According to the slope of the initial portion of these isotherms, the affinity increases as the organic matter content increases. They calculated the adsorption capacity ( $K_f$ ) of the samples for the herbicide diuron, the experimental data points were fitted to the Freundlich equation. The  $K_f$  values ranged between 2.17 mg kg<sup>-1</sup> for the original soil (containing 0.18% OC) and 34.28 mg kg<sup>-1</sup> for the peat-amended sample containing 4.61% OC. The breakthrough curves and distribution of diuron along the soil profile, obtained from the step-function type and pulse type experiments by using the soil column studies, indicate that the amount of diuron retained ranged from 359.3 mg kg<sup>-1</sup> for the column filled with the original soil to 439 mg kg<sup>-1</sup> for that filled with the peat-amended soil containing 4.61% OC. The amount of diuron desorbed (373.0 mg kg<sup>-1</sup>) from the soil containing the higher percentage of organic carbon (4.61%) was greater than that desorbed (300.8 mg kg<sup>-1</sup>) from the original soil, which might be due to the joining of diuron to the soluble fraction of the organic matter moving through the column (Gonzalez-Pradas et al., 1998).

Goody and coworker (2002) studied to assess the degradation, fate and transport of diuron and its metabolites in calcareous soil in southern England. An agricultural grade of diuron was applied to the soil surface at a rate of 6.7 kg/ha along with a potassium bromide conservative tracer applied at 200 kg/ha, in early January, 2001. Hand augured samples were taken at regular intervals over the next 50 days,

samples collected down to 54 cm. Porewaters were extracted from the soil cores by using high speed centrifugation and the supernatant fluids were retained for analysis by HPLC, for diuron and three of its metabolites, *N'*-[3,4-dichlorophenyl]-*N,N*-methylurea (DCPMU), *N'*-3,4-dichlorophenylurea (DCPU) and 3,4-dichloroaniline (DCA). The centrifuged soil was retained and then extracted with methanol prior to HPLC analysis for the same suite of phenylureas. A mass balance approach showed large variations in diuron distribution, but on average accounted for 104% of the diuron applied. Concentrations of diuron and its metabolites were roughly five times higher in the soil than in the soil porewaters. After 50 days, metabolites comprised 10% of the total diuron present in the porewater and 20% of the total diuron sorbed to the soil matrix. After 36 days, a large pulse of diuron and DCPMU appeared in the porewaters and soil matrix at a depth of 54 cm, travelling an average of 0.15 cm/day faster than Br. A preferential route for diuron transport is suggested. There is evidence to suggest that degradation occurs at depth as well as at the soil surface. Metabolites generally appear to move more slowly than the parent compound. All metabolites were encountered, but interpreting transport and degradation processes simultaneously proved beyond the scope of the study. Diuron was detected once in a shallow (5 m) observation well, situated on the experimental plot. High concentrations of diuron and metabolites were still present in the soil and soil solutions after 50 days and remain as a source of potential groundwater contamination (Goody et al., 2002).

Chu and Kwan (2003) provided new information regarding the soil-washing of chlorinated hazardous materials in a surfactant/organic solvent system, which has not been studied before. This study investigates a new approach using a solvent/surfactant-aided soil-washing process to improve the performance of

conventional surfactant-aided soil remediation. Three surfactants (Brij 35, Tween 80, and SDS) and three organic solvents (acetone, triethylamine, and squalane) were used to evaluate the desorption performances of 4,4'-dichlorobiphenyl (DCB) out of three soils with different sorption characteristics. The performance improvement is likely due to better dissolution of the hydrophobic contaminants from the soil assisted by the solvent, and the formation of solvent-incorporated surfactant micelles, which increases both the size (i.e. capacity) and affinity of micelles for more effective contaminant extraction. The fraction of organic carbon ( $f_{oc}$ ) expressed as a percentage of the weight of organic carbon over the total soil weight of each sample. The  $f_{oc}$  of soils were found to be important in determining the performance of a solvent/surfactant-aided soil-washing process. Judging from the experimental data and as verified by the two constants in the proposed soil-washing model, as the organic solvent is coexisting with the surfactant micelles, both the marginal soil-washing performance (right after the use of a very small amount of solvent compared to that of none) and the final soil-washing capacity were increased about 82-99% compared to those of a pure surfactant-aided washing process (Chu and Kwan, 2003).

Walker and coworker (2005) investigated the variations in leaching losses of some soil applied herbicides (chlorotoluron, isoproturon and triasulfuron) from small intact columns of a structured clay loam and an unstructured sandy loam soil that were measured in five separate field experiments, and gain further information concerning the factors influencing the availability of pesticides for movement in soils. In general, losses of all three herbicides were greater from the clay loam than from the sandy loam soil and the order between herbicides was always triasulfuron >> isoproturon > chlorotoluron. Differences between experiments were also consistent for every soil/herbicide combination. There was no relationship

between total loss and either total rainfall or cumulative leachate volume. When weighting factors were applied to the rainfall data to make early rainfall more important than later rainfall, there were significant positive relationships between cumulative weighted rainfall and total losses. Also, there were significant negative correlations between total losses and the delay to accumulation of 25 mm rainfall (equivalent to one pore volume of available water) in the different experiments. In laboratory incubations, there was a more rapid decline in aqueous (0.01 M calcium chloride) extractable residues than in total solvent extractable residues indicating increasing sorption with residence time. However, the rate of change in water extractable residues could not completely explain the decrease in leachability with aging of residues in the field. Short-term sorption studies with aggregates of the two soils indicated slower sorption by those of the clay loam than by those of the sandy loam suggesting that diffusion into and out of aggregates may affect availability for leaching in the more structured soil. Small scale leaching studies 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 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 ageing of residues (Walker et al., 2005).

Sheng and coworker (2005) evaluated the influence of pH on the sorption of diuron, bromoxynil and ametryne by a soil in the presence and absence of a wheat residue-derived char. The sorption was measured at pHs ~3.0 and ~7.0. Wheat char was found to be a highly effective sorbent for the pesticides, and its presence (1% by weight) in soil contributed >70% to the pesticide sorption (with one exception). The sorption of diuron was not influenced by pH, due to its electroneutrality. Bromoxynil

becomes dissociated at high pHs to form anionic species. Its sorption by soil and wheat char was lower at pH ~7.0 than at pH ~3.0, probably due to reduced partition of the anionic species of bromoxynil into soil organic matter and its weak interaction with the carbon surface of the char. Ametryne in its molecular form at pH ~7.0 was sorbed by char-amended soil via partitioning into soil organic matter and interaction with the carbon surface of the char. Protonated ametryne at pH ~3.0 was substantially sorbed by soil primarily via electrostatic forces. Sorption of protonated ametryne by wheat char was also significant, likely due not only to the interaction with the carbon surface but also to interactions with hydrated silica and surface functional groups of the char. Sorption of ametryne by char-amended soil at pH ~3.0 was thus influenced by both the soil and the char (Sheng et al., 2005).

Rodriquez-Cruz and coworker (2006) studied the efficiency of two surfactants, one anionic (SDS) and other non-ionic (Triton X-100), in the desorption of atrazine and linuron after 0, 3, and 9 months of soil-herbicide aging time. Batch desorption studies were conducted in soil-water and in soil-water-surfactant systems. The kinetic pattern of desorption was biphasic, a slow desorption following an initial fast phase. Both phases followed first-order kinetics. The desorption rate of the first phase (K1) was very low in water for both herbicides and always increased in the presence of 10- and 100-fold of critical micelle concentration (CMC) for SDS and Triton X-100, respectively. At zero time, desorption rate increased 9- and 8-fold (atrazine) and 24- and 17-fold (linuron) in the presence of the two surfactants, respectively. Desorption rates decreased with the increase in the aging time in all three desorption systems. After 9 months of soil-herbicide aging time, DT25 (parameters relative to the required for desorption of 25%) for linuron was 6.85 h (SDS) and 41.7 h (Triton X-100) and for the atrazine it was only possible determine in SDS solution (17.2h) because it was

not possible to calculate in water since 25% of desorption was not reached in the first phase of the kinetic, whereas in Triton X-100 solution DT25 was only attained after 3 months of aging time and it was not possible to archive this desorption after 9 months of sample incubation. The amount of desorbed herbicide in the different systems varied from 35.6-12.5% (water), 87.9-46.2% (SDS), and 63.2-18.0% (Triton X-100) for atrazine and 8.02-3.94% (water), 69.9-41.3% (SDS), and 58.1-34.8% (Triton X-100) for linuron. The ratio of amount desorbed in surfactant solution and in water for the different aging times of the herbicides was greater for the desorption of linuron than that of atrazine. For both herbicides, the desorption was always greater with SDS than with Triton X-100, and was higher when it was used for desorption of the residues aged for 9 months. The results indicated the interest of surfactants for increasing the desorption of atrazine and linuron from soils polluted with these compounds after a long aging time in the soil. Therefore, they suggested the possibility to use the pump-and-treat remediation technique for pesticides in soils with a long history of pollution. The enhanced desorption achieved will be governed by the hydrophobic character of the herbicide, the nature of the surfactant used, the aging time, and the characteristics of soils (Rodriguez-Cruz et al., 2006).

Hincapie and coworker (2005) evaluated two well-defined advanced oxidation processes (AOPs) systems in a large pilot plant. The processes were applied to the degradation of the six pesticides (alachlor, atrazine, chlorfenvinphos, diuron, isoproturon and pentachlorophenol) considered priority substances (PS) by the European Water Framework Directive WFD. The efficiency of both treatment methods was evaluated not only for pesticide degradation and mineralization, but also water toxicity at different stages of treatment. These pesticides were dissolved in water at 50 mg/L (or at maximum water solubility) and were degraded at pilot plant

scale using photo-Fenton and TiO<sub>2</sub> photocatalysis driven by solar energy. Two different iron concentrations (2 and 55 mg/L) and TiO<sub>2</sub> at 200 mg/L had been tested, using mainly total organic carbon (TOC) mineralisation for comparison of treatment effectiveness. *Vibrio fischeri* (Microtox1) toxicity assays were also employed for evaluating the photocatalytic treatments and comparison between these results and parent compound disappearance, TOC evolution and anion (or ammonia) release were discussed. Almost complete mineralisation and total detoxification were always attained. It has been demonstrated that evolution of chloride could be a key-parameter for predicting toxicity of chlorinated compounds (Hincapie et al., 2005).

Chan and Chu (2005) investigated the photolytic destruction of Atrazine (ATZ) following a surfactant-aided soil-washing process in the presence of humic acid (HA). They used different concentrations (0.007-0.02 M) of Brij 35, non-ionic surfactant, to extract ATZ without causing any retardation effect on the photolysis process. However, the HA that was co-extracted from the surfactant-aided soil-washing system was found to be capable of improving the photolysis of ATZ at low concentrations, while quenching the photodegradation of ATZ at higher concentrations. By considering the light attenuation affects due to surfactant and HA, the quantum yields of the system with respect to the proposed reaction mechanisms of the associated excited states of ATZ were investigated and modeled. The relative kinetic rates of the dominant reaction mechanisms (i.e., deactivation of triplet, direct photolysis of triplet, product formation, and quenching of triplet) were then compared (Chan and Chu, 2005).

Klongdee and coworker (2005) synthesized nanoparticles of anatase titania by the thermal decomposition of titanium (IV) n-butoxide in 1,4-butanediol. The powder obtained was characterized by various characterization techniques, such as XRD,



BET, SEM and TEM, to confirm that it was a collection of single crystal anatase with particle size smaller than 15 nm. The synthesized titania was employed as catalyst for the photodegradation of diuron, a herbicide belonging to the phenylurea family, which has been considered as a biologically active pollutant in soil and water. Although diuron is chemically stable, degradation of diuron by photocatalyzed oxidation was found possible. The conversions achieved by titania prepared were in the range of 70–80% within 6 h of reaction, using standard UV lamps, while over 99% conversion was achieved under solar irradiation. The photocatalytic activity was compared with that of the Japanese Reference Catalyst (JRC-TIO-1) titania from the Catalysis Society of Japan. The synthesized titania exhibited higher rate and efficiency in diuron degradation than reference catalyst. The results from the investigations by controlling various reaction parameters, such as oxygen dissolved in the solution, diuron concentration, as well as light source, suggested that the enhanced photocatalytic activity was the result from higher crystallinity of the synthesized titania (Klongdee et al., 2005).

## 2.2 Background

### 2.2.1 Diuron

**Synonyms:** *N'*-(3,4-Dichlorophenyl)-*N,N*-dimethylurea; 3-(3,4-Dichlorophenyl)-1,1-dimethylurea; DCMU; DMU

**Chemical abstract number (CAS#):** 330541

**Molecular formula:** C<sub>9</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>O (233.1)

**Trade names and available formulations:** Karmex, Karmex DL, Diuron 80WP, Diuron 4L, Direx 4L, Di-on, Diurex, Duriol, Dailon, Rout, Diater, Unidron, Crisuron, and Cekiuron.

### Physical and chemical properties

Diuron is a colorless crystalline compound in its pure form, non-ionic with a moderate water solubility of  $42 \text{ mg l}^{-1}$  at  $20^\circ\text{C}$ . It remains as a solid at ambient temperature with a melting point of  $158 - 159^\circ\text{C}$ . Vapor pressure is  $0.009 \text{ mPa}$  at  $25^\circ\text{C}$  and a calculated Henry's law constant of  $0.000051 \text{ Pa m}^3 \text{ mol}^{-1}$  suggesting that diuron is not volatile from water or soil.

The rate of its hydrolysis is negligible at neutral pH but increases as the conditions become strongly acidic or alkaline (Salvestrini et al., 2002); leading to its principal derivative, 3,4-DCA. It has a low to moderate octanol-water partition coefficient ( $\log K_{ow} = 2.6$ ). This compound has a soil-organic fraction partition constant of 485 which predicts its adsorption affinity to soil organic particles. This high value of  $K_{oc}$  shows a high adsorption capacity and, therefore, a heterogeneous repartition in soil.

### Usage

Diuron was introduced in 1954 by E.I. Du Pont de Nemours & Co. (Inc.) under the trademark "Karmex" and is mainly used as a pre-emergence herbicide for general weed control on noncrop lands. It is also used as a soil sterilant. The industrial use of diuron, for example, along railroad rights-of-way, represents 57% of the total usage. As of 1995, the estimated usage of diuron in the United States was about 2-4 million pounds (Aspelin, 1997). Diuron is also used selectively before emergence on crops such as asparagus, citrus, pineapple, sugarcane, and cotton. As a photosynthesis inhibitor (Figure 2.1), diuron injures weeds with symptoms of foliar chlorosis concentrated around veins (sometimes interveinal) followed by necrosis (Sheng et al., 2005). Tolerance for diuron residues was established at 1 ppm on fruits and vegetables in Canada (Chapman, 1967). The occupation exposure limit (TWA, i.e., 8-hour time-weighted average) for diuron in workplace air was established at  $10 \text{ mg m}^{-3}$  by

ACGIH in the United States (International Labor Office, 1980), which indicates that occupational intake at a rate of  $1.4 \text{ mg kg}^{-1} \text{ day}^{-1}$  is considered safe (Stevens and Sumner, 1991). Diuron has been also used on non-crop areas such as roads, garden path and railway lines at  $3 \text{ kg ha}^{-1} \text{ year}^{-1}$  and on many agriculture crops at  $1.8 \text{ kg ha}^{-1} \text{ year}^{-1}$ . In France, where its use has been limited since 1999, about 109 tons were manufactured in 1996 and 133 tons in 1997 (Giacomazzi and Cochet, 2004).

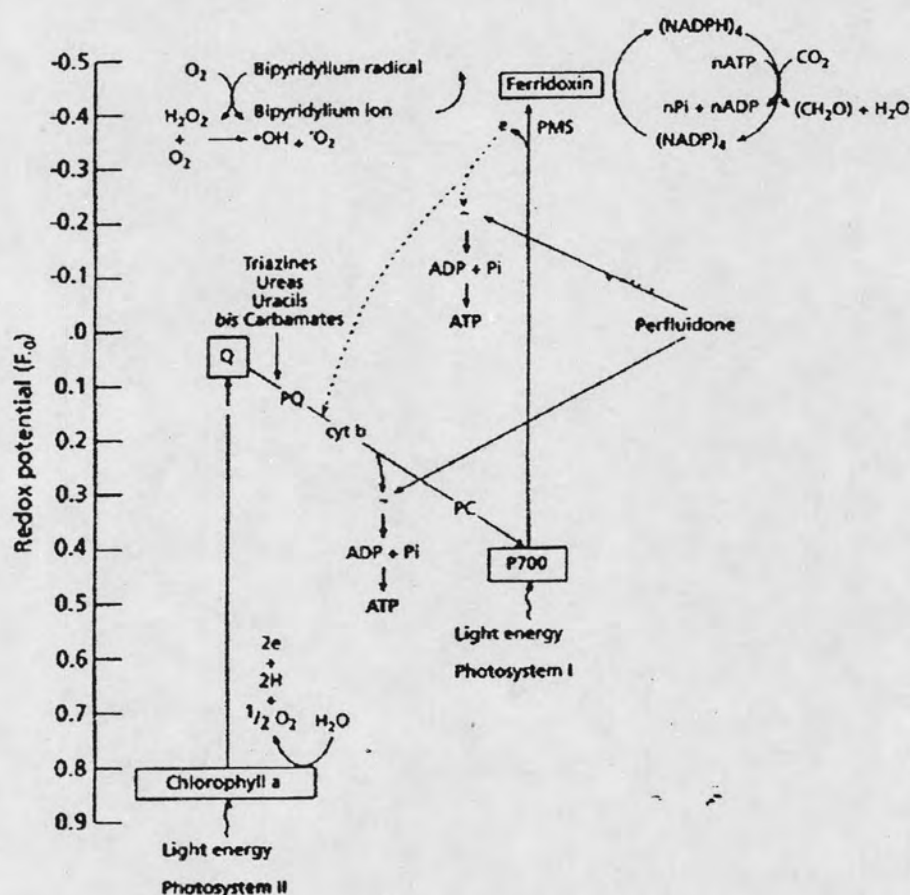


Figure 2.1 Photosynthesis inhibition by diuron

### Diuron in environment

Due to its high persistence (one month to one year), diuron can be found in many environment such as soil, sediments and water (Field et al., 2003).

In soil, considering its low volatility and its high  $K_{oc}$ , diuron is found in the solid phase rather than in the gaseous or liquid phase. Sorption studies of diuron have shown that the proportion of organic matter in soil directly influences the amount of adsorbed diuron (Alva and Singh, 1990). These authors also showed that diuron was subjected more to leaching in deeper soil because of the small amount of organic matter. In the upper 25 cm of the soil, the quantity of diuron leached ( $0.08 \mu\text{g g}^{-1}$ ) was lower than in the deeper layer (at 120 cm,  $0.45 \mu\text{g g}^{-1}$ ) giving rise to an easier pollution of water.

In another study, residues of diuron were analyzed in a soil in New Zealand after 13 years of annual application of  $4.5 \text{ kg ha}^{-1} \text{ year}^{-1}$ . It was shown that residual concentration decreased with depth and totally disappeared after 70 cm (Tworkoski et al., 2000). However, this phenomenon seems to depend on soil structure. In a calcareous soil, diuron and its metabolites could be found in excess at a depth of 50 cm in eight days in both pore waters and sorbed to the soil matrix (Goody et al., 2002). Total dissipation of diuron appeared after 125 days in the upper 10 cm. It was also demonstrated that in a loam non-treated soil, the half life of diuron, in the first 10 cm, was 81 days. However, when this soil is treated for 12 years with the same amount of diuron ( $3 \text{ kg ha}^{-1} \text{ year}^{-1}$ ), the half life decreases to 37 days. Thus, diuron produced a moderately enhanced biodegradation, which was not observed with other herbicides (Rouchaud et al., 2000). These results are in accordance with those of Sheets (Sheets, 1964) who was the first to present the evidence of the role of microorganisms. In his study, he showed that after a treatment of 2-4 years with 2.2- $4.5 \text{ kg ha}^{-1}$ , no accumulation of diuron could be detected.

*N*-phenylurea herbicides seem to be degraded in soil but it must be kept in mind that this biotic or abiotic degradation could lead to accumulation of very toxic

derived compounds. Diuron dissipation could also be imputed to leaching due to intensive rainfall, then leading to a main cause of groundwater pollution (Goody et al., 2002). Diuron is also a source of pollution in aquatic environment because of its use as antifouling paint biocide. In Japanese aquatic environment, 86% of samples studied showed a  $3.05 \mu\text{g l}^{-1}$  concentration of diuron (Okamura et al., 2003). In Dutch coastal and marinas waters, a higher level than the permitted maximum of  $430 \text{ ng l}^{-1}$  was detected (Lamoree et al., 2002). Diuron and diuron degradation products were detected in surface waters and in the bottom sediments (Thomas et al., 2002), but few data were reported on the in situ biodegradation. In laboratory, diuron showed no biodegradation over 42 days in seawater at  $15^\circ\text{C}$  while the degradation products of diuron were less persistent (Thomas et al., 2002).

Diuron was found present mainly in seawater (Voulvoulis et al., 2002) and it was shown that an increase in particulate matter concentration enhances sorption of diuron to marine sediments (as compared to the other biocides). This phenomenon appears to be slightly irreversible. Dispersion of this compound in agriculture leads to pollution of the aquatic environment by soil leaching (Thurman et al., 2000). Diuron is considered a Priority Hazardous Substance by the European Commission, Drinking Water Directive 80/778 indicates a maximum amount of  $0.5 \mu\text{g l}^{-1}$  of total herbicide and  $0.1 \mu\text{g l}^{-1}$  for each constituent. No concentration is given for other surface water (Malato et al., 2002). According to the French Environmental Institute (IFEN, 1998), diuron is detected in 28% of the samples from rivers in the national basin system (Giacomazzi and Cochet, 2004).

#### **Diuron in Thailand**

Contaminations of soil and water in Thailand by organochlorine pesticides have been monitored since 1974. In Thailand, application of the pre-emergence

herbicide Diuron, at the rate of 1.5 kg/ha during the land preparation for plantation of several economically important crops in Thailand such as cassava, sugarcane, and pineapple. In 2001, the estimated imported of diuron in Thailand was about 65 tons (about 140 million baht) (Chinawong and Suwanketnikom, 2001).

### **Toxicity and ecotoxicity of diuron**

#### **(i) Health effects on mammals**

Diuron is absorbed from the gastrointestinal and respiratory systems. In humans, it is metabolized within hours by hydroxylation and N-dealkylation, then excreted via the urine (Hayes Jr., 1982). In rats and dogs, one-sixth to one-half of the total elimination was found in the faeces. Following the ingestion of diuron of nine months to two years by rats and dogs, little storage was observed in any tissue with the highest levels seen in the liver and kidney (Hodge et al., 1967)

#### ***Acute toxicity***

Diuron seems to be slightly toxic to mammals. Juveniles and animals on protein-deficient diets are more susceptible than adults to the toxic effects of diuron based on the LD<sub>50</sub> (Hayes Jr., 1982). The oral LD<sub>50</sub> in rats is 3.4 g kg<sup>-1</sup>. The dermal LD<sub>50</sub> is greater than 2 g kg<sup>-1</sup>. (EXTension TOXicology NETwork: <http://ace.orst.edu/info/extoxnet/ghindex.html>). Some signs of central nervous system depression have been observed at high levels of diuron exposure but the principal toxic effects of chronic ingestion of diuron were weight loss and abnormalities in blood, liver and spleen. No significant symptoms could be observed after oral exposition of human to diuron.

#### ***Chronic toxicity***

Two main chronic feeding studies have been conducted with diuron. The first part of the study was conducted for two years by administering diuron into the diet of

two male and three female beagle dogs at dose levels corresponding to 0, 0.625, 3.125, 6.25 or 31.25 mg kg<sup>-1</sup> bw day<sup>-1</sup>. The second part of the study was conducted on 35 rats of each sex at dose levels corresponding to 0, 1.25, 6.25, 12.5 or 120 mg kg<sup>-1</sup> bw day<sup>-1</sup> (Hodge et al., 1967). At 125 ppm (corresponding to 3.125 mg kg<sup>-1</sup> bw day<sup>-1</sup> in dogs and 6.25 mg kg<sup>-1</sup> bw day<sup>-1</sup> in rats), traces of abnormal blood pigments were observed in a few animals but were not significant. At 250 ppm and above haemolytic alterations, weight loss, haemosiderosis of the liver and erythroid hyperplasia were observed. The no-observed-adverse-effect level (NOAEL) was 125 ppm. Although there was no evidence of carcinogenicity in these experiments.

#### *Reproductive effects*

Daily low doses of diuron fed to female rats through three successive generations resulted significantly in a decreased body weight of offspring in the second and third litters. However, the fertility rate do not seem to be affected by diuron (Hayes Jr., 1982).

#### *Teratogenic effects*

Diuron is teratogenic at high doses. Administered to pregnant rats from day 6 to 15 of gestation, it did not produce any birth defects in the offspring in doses of up to 125 mg kg<sup>-1</sup> day<sup>-1</sup>. However, doses of 250 mg kg<sup>-1</sup> day<sup>-1</sup> caused wavy ribs, extra ribs and delayed bone formation (Medicine, 1995).

#### *Mutanogenic, Carcinogenic and organ effects*

In most microbial tests performed, diuron was found to be non-mutagenic with or without metabolic activation and in one strain, *Salmonella typhimurium*, it was even activated (Seiler, 1978). There exists limited evidence to indicate that low level of exposure to diuron does not cause cancer (Agency, 1983).

#### *(ii) Ecological effects*

Diuron is slightly toxic to birds. In bobwhite quail LC50 is 1730 ppm. In Japanese quail and ring-necked pheasant, it is greater than 500 ppm. On aquatic organisms LC50 (48 h) values for diuron range from 4.3 to 42 mg l<sup>-1</sup> in fish and range from 1 to 2.5 mg l<sup>-1</sup> in aquatic invertebrates. The LC 50 (96 h) is 3.5 mg l<sup>-1</sup> for rainbow trout. Thus diuron is moderately toxic to fish and slightly toxic to aquatic invertebrates. Toxicity of diuron has been studied in many organisms such as worms and snails, frogs and goldfish. For worms (*Lumbriculus variegatus*) and snails (*Physa gyrina*), no LC50 could be determined but effects on weight and growth were observed, respectively, at 29.1 and 15.3 mg l<sup>-1</sup> for worms and snails (Nebeker and Schuytema, 1998). A previous study showed a LC 50 96 h for *Lymnea* spp. (snails) at the same concentration of diuron (15.3 mg l<sup>-1</sup>) (Christian and Tate, 1983). On frogs, diuron showed effects on survival, growth and malformations in laboratory where concentrations used were higher than in normal field conditions (Schuytema and Nebeker, 1998). On goldfish, exposure to very low concentration (5 µg l<sup>-1</sup>) as detected in the environment (Okamura et al., 2003), during 24 h, induce a variety of significant behavioral alterations, more particularly by altering the chemical perception of natural substance of eco-ethological importance (Saglio and Trijasse, 1998).

Negative effects of diuron at 25 mg l<sup>-1</sup> on bacterial community structure and on bacterial activity have also been shown (El Fantroussi et al., 1999). El Fantroussi et al. (1999) showed by PCR-DGGE technique that bacterial diversity seemed to decrease in soil treated by diuron or other phenylurea herbicides. Sequence determination of several fragments obtained in DGGE revealed that the most affected species in diuron treated soil belonged to an uncultivated bacteria group. Another study showed that microbial activity is reduced by the presence of diuron. The activity



is decreased by the use of immobilised diuron on silica particles (Prado and Airlodi, 2002).

### 2.2.2 Contaminant Adsorption Isotherm

The adsorption of contaminant from solution onto a solid occurs as the result of one of two characteristic properties for a given solvent-solute-solid system, or a combination thereof. The primary driving force for adsorption may be a consequence of lyophilic (solvent-disliking) character of the contaminant relative to the aqueous phase, or off a high affinity of the contaminant to the solid.

The degree of solubility of a dissolved substance is by far and most significant factor in the intensity of the first of the two driving forces. The more the contaminant likes the solvent, the more hydrophilic in the case of an aqueous solution, the less likely it is to remove toward an interfacial to be adsorbed. Conversely, a hydrophilic (water disliking) substance will more likely be adsorbed from aqueous solution (Weber, 1970).

When the measured adsorption data are plotted against the concentration value of the adsorbate at equilibrium, a graph is obtained called the adsorption isotherm. A useful relation between the shape of the adsorption isotherm and the adsorption mechanism for a solute-solvent adsorbent system is based on the classification of Giles et al. (Giles et al., 1960). This design classified adsorption patterns of soils in four different categories. The different isotherms included the S, C, L, and H-type isotherms as follows:

The S-curve isotherm is characterized by an initial slope that increases with the concentration of a substance in the soil solution. This type occurs where lower concentrations of the pesticide remain in water, mid-level concentrations adsorb, and

high concentrations reach a maximum adsorption. This suggests that the relative affinity of the soil solid phase for the solute at low concentration is less than the affinity of the soil for the solvent

The C-curve isotherm exhibits an initial slope that remains independent of the substance concentration in the solution under the possible experimental condition. This type of isotherm looks like a constant partitioning of solute between the solvent and the adsorbing surface. It may be due to a proportional increase of the adsorbing surfaces as the surface excess of an adsorbate increases.

The L-type isotherm (Langmuir) is characterized by an initial slope that does not increase with the concentration of the substance in the soil solution. This behavior points out the high relative affinity of the soil solid phase at low concentration and a decrease of the free adsorbing surface.

The H-type isotherm (high affinity) is characterized by a large initial slope which indicates the high affinity of the soil solid phase on the adsorbate. This type is similar to the L-type but has a higher affinity at low concentrations and reaches a maximum

Depending on their molecular properties and the properties of the solvent, both inorganic and organic pollutants exhibit adsorption isotherms fitting one of Giles' isotherm classifications. These isotherms can describe the adsorption mechanism of potentially toxic organic compounds as controlled by the properties of the adsorbent, properties and concentration of the solute, and characteristic of the solvent (Weber, 1970).

The difference between the amount of an herbicide adsorbed to a soil or sediment and the amount of the herbicide desorbed from the same soil or sediment is known as hysteresis. No one mechanism influences the adsorption and desorption

process of a compound in the same way. Several types of bonds, varying in strength between the sediment and herbicide, can cause adsorption. The same bonds influences the herbicides desorption. Bonds range from weak bonds such as London-van der Waals forces to strong bonds such as covalent bonds. In desorption, the weaker bonds are broken, but the stronger ones may not be over come. Without the release of these stronger bonds, equilibrium during the desorption process is never met. This in part explains the amount of certain herbicides, which remain adsorbed even after several desorption cycles (Koskinen and Harper, 1990).

Contaminant adsorption isotherms are frequently described by the Freundlich equation. The Freundlich equation was empirically driven to allow for the logarithmic decrease in adsorption energy with increasing coverage of the adsorbent surface. Freundlich found that adsorption data for many dilute solutions could be fitted by the expression

$$C_s = K_f C_w^n$$

Where  $K_f$  and  $n$  are empirical constants and the other terms are defined above

The Freundlich isotherm can be written in form of a linear equation as

$$\text{Log } C_s = \text{log } K_f + n \text{ log } C_w$$

Where:  $C_s$  = total adsorbate concentration associated with the adsorbent, mg/g solid

$C_w$  = equilibrium concentration of the adsorbate in the solution, mg/l

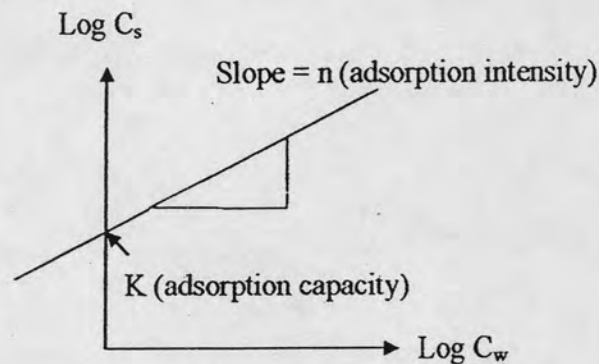
$K_f$  = Freundlich constant, mg/g solid

$n$  = a constant which is a measure of the nonlinearity of the isotherm, 1/g solid

$K_f$  and  $n$  are empirical constants characteristic of the contaminant and solid used. If plotted,  $K_f$  is the intercept of the isotherm at  $C_w$  equal to 1 and  $n$  is the slope of the line when the equation is plotted on the logarithmic paper (Figure 2.2). The

intercept shows the adsorption capacity while the slope is proportional to the adsorption intensity (Dobbs and Cohen, 1980). When  $n < 1$ , adsorption affinity decreases with an increasing concentration. In case of  $n = 1$  affinity of the solid for the sorbate remains the same for all level of  $C_s$ . Finally, in the case of  $n < 1$ , a modification of the surface occurs resulting in increased affinity for the surface (Weber, 1970).

The main limitation of the Freundlich equation is the fact that it does not predict a maximum adsorption capacity. However, in spite of its limitations, the Freundlich equation is widely used for describing pollutant adsorption on the soil solid phase.



**Figure 2.2** A relationship between concentration of a contaminant in the sorbed state ( $C_s$ ) and the dissolved state ( $C_w$ ).

### 2.2.3 Soil Washing

An important environmental concern with pesticides is their potential to move through soils and to contaminate surface water via drainflow, or deeper groundwater resources by percolation through subsoils and the deeper soil horizons. There is considerable variation in the extent of pesticide movement through soils as a result of variation in (i) soil properties that control water movement, (ii) pesticide/soil

interactions that control availability for movement, (iii) weather patterns, particularly rainfall, that control the timing of major leaching events (Walker et al., 2005). The leaching of phenylurea herbicides into groundwater from agriculture areas receives increasing attention. Adsorption and desorption behavior of pesticide by active soil surfaces are related to the structure of the organic substances and the chemical composition of the soil solution, and influence the migration behavior of organic pesticides (Borisover and Graber, 1997)

Therefore to protect contamination in groundwater and soil, soil washing is a treatment process used for remediation both organic and inorganic chemical constituents from contaminated soils, sludge, and sediments such as semi-volatile and non-volatile organic compounds, dioxins, furans, pesticides, petrol hydrocarbons, poly-nuclear aromatic compounds, and PCB. Soil washing has been used in Europe to clean up radioactive wastes but removal is not always complete. This process involves high energy contact between the contaminated soils and an aqueous based washing solution. Soil washing can be a physical and/or chemical process which results in the separation, segregation and volume reduction of hazardous materials and/or the chemical transformation of contaminants to nonhazardous, unregulated substances.

The steps involved in soil washing are:

- (1) Excavation of the contaminated soil
- (2) Remedial treatment of the contaminated soil
- (3) Solid/liquid separation of all contaminants;
- (4) Treatment or disposal of all residues
- (5) Final soil deposition.

Large debris or soil particles coarser than 2 inch. are separated out before treatment begins. Cobbles and stones are separated from silts and clays. The soil then

enters a soil scrubbing unit. The soil portion containing sand needs only initial rinsing treatment because contaminants do not strongly adhere to the sand particles. The silt/clay fractions needs more extensive remedial treatment because contaminants are easily sorbed by this fine-grained soil fraction, and consequently, are more difficult to desorb. The solid/liquid separation process then takes place, and the contaminated wastewater containing residues is treated in a conventional wastewater treatment system and recycled. At this stage, the contaminants have either been destroyed or are isolated and removed. The last step in the soil washing process is the redeposition of the remediated soil in the appropriate location (Figure 2.3) (Agency, 1990).

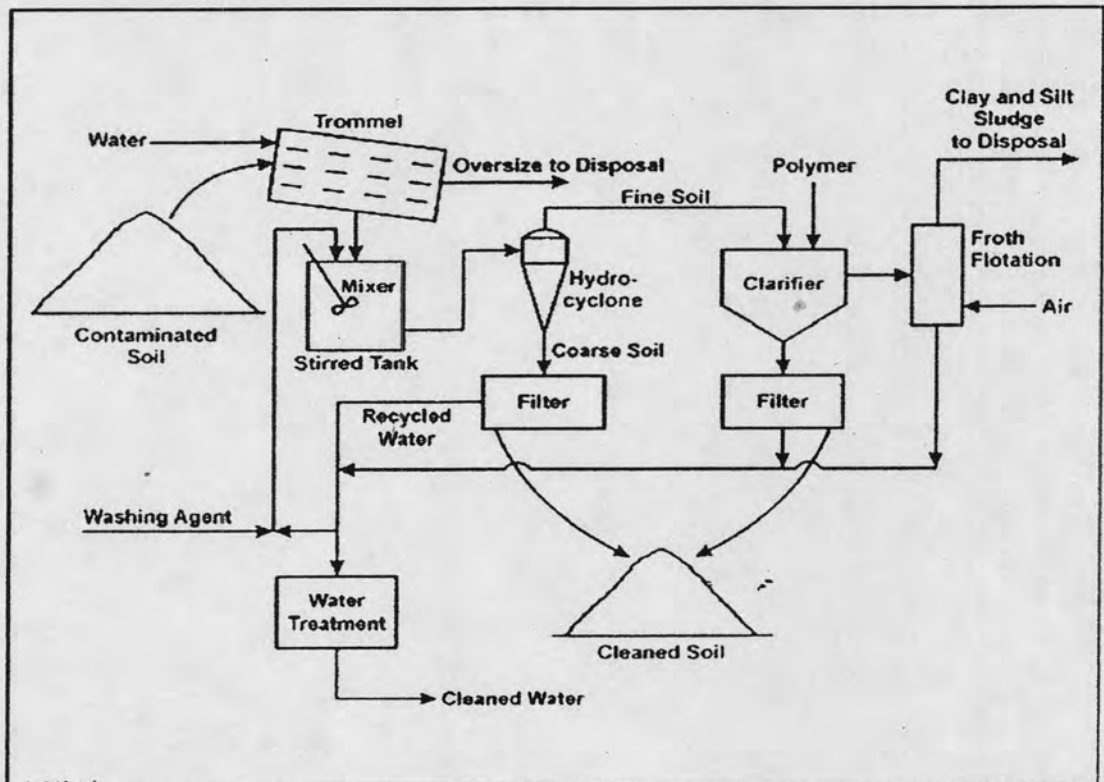


Figure 2.3 Step of soil washing.

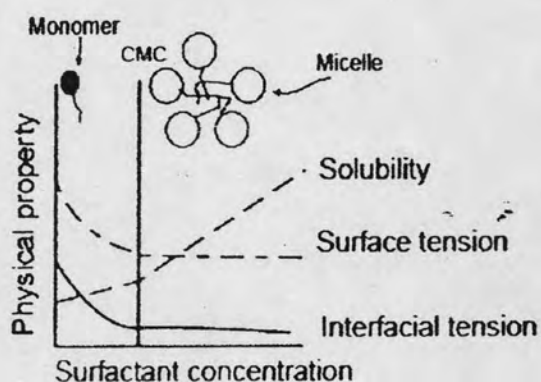
The effectiveness of soil washing is dependent on the soil type and contaminants that it contains. Soil washing is most effective for removing halogenated

volatiles, nonhalogenated volatiles, and metals contained in sandy and gravelly soils. However, the applicability of this procedure must be tested when the soils are classified as silt or clay because soil washing is not considered effective when soils contain more than 20-30% silt/clay. The type of extractive agent needed for the specific soil washing process depends on the class of contaminant and the soil type. Water washing with a basic or surfactant agent is used to remove organics. The types of basic aqueous solutions used as extractive agents include caustic lime, slaked lime, or industrial alkali-based washing compounds. An acidic or chelating agent is used to remove organics and heavy metals. Acidic aqueous solutions used as extractive agents include sulfuric, hydrochloric, nitric, phosphoric, and carbonic acids. Oxidizing agents, such as hydrogen peroxide and sodium hypochlorite, chemically change the contaminants and often facilitate the washing process. Organic-solvent washing agents are used to remove hydrophobic organics and PCBs (Agency, 1988).

There are numerous advantages to soil washing as a remediation technique. First, the actual process takes place in a closed system which permits control of the ambient environmental conditions. Secondly, the process can result in a significant volume reduction of the contaminant mass. Also, soil washing has extensive applications for varied waste groups, and the hazardous waste can remain on site due to mobile technology. The costs of soil washing are relatively low compared to other multi-contaminant technologies and significantly lower than the cost of land filling. Soil washing also has disadvantages as a remediation procedure. When the soil washing treatment is only a physical process, there is little reduction in the toxicity of the contaminants. If chemical processes are involved, potentially hazardous chemicals that are used in the remediation process may then be difficult to remove from the treated soil and may remain on site. The effectiveness of soil washing is also limited

by the following factors: (1) complex waste mixtures, (2) high humic content of soils, (3) inhibiting solvent-soil reactions, and (4) high fine-grained clay content of soils (Raghavan et al., 1990).

Surfactants are chemicals with polar and non-polar regions (amphiphilic compounds) that are classified based on the net charge of the hydrophilic head group (anionic, cationic, zwitterionic). Surfactant can reduce the free energy of the system by replacing the bulk molecules of higher energy at an interface. They contain a hydrophobic portion with little affinity for the bulk medium and a hydrophilic group that is attracted to the bulk medium. Surfactant monomers will form spheroid or lamellar structures with organic pseudo phase interiors. This coincides will lower surface and interfacial tensions (Figure 2.4) (Rosen, 1978). At bulk solution concentrations of a given surfactant greater than a specific threshold value, known as the critical micelle concentration (CMC), the hydrophobic moieties of the surfactant molecules are attracted to each other in bulk solution and create aggregates termed micelles.



**Figure 2.4** Schematic diagram of the variation of surface tension, interfacial and contaminant solubility with surfactant concentration.



One way of characterizing the efficiency of a surfactant as emulsifier is the Hydrophilic-Lipophilic Balance, HLB. This means the balance between the oil soluble and water soluble moieties in a surface active molecule (a relative ratio of polar and non-polar groups in the surfactant). This method was developed by Griffin in 1949 and has been proved very successful with alkoxyated non-ionic surfactants but less successful with ionic surfactant. High HLB-numbers indicate water-soluble surfactants, whereas low HLB-numbers indicate water-insoluble surfactants. The HLB numbers of surfactants depend on the oil type as well as the solution temperature. The surfactant used would help to form the micro emulsion. It is desirable that the surfactant used in the formulation is anionic or nonionic. HLB number is ranging from 0-40; can be assigned to a surfactant, based on emulsification data. As the surfactant goes from the water phase (hydrophilic) to the oil phase (lipophilic), the hydrophilic-lipophilic balance (HLB) decreases. Thus, surfactants with high values of HLB are highly water soluble.

- *Strongly hydrophilic surfactant*, HLB  $\rightarrow$  40

- *Strongly lyophilic surfactant*, HLB  $\rightarrow$  1

The HLB value of the surfactants can be calculated, for example, as follows:

The HLB value of a polyoxyethylene (POE) nonionic surfactant is calculated by the following equation:  $HLB\ value = E/5$

where E is a value of percent by weight of an ethylene oxide group moiety

"POE" means polyoxyethylene, each value in parentheses means the average added mole number in the case of POE or the average molecular weight in the case of polyethylene glycol. Ethylene oxide molecules are often inserted at active hydrogen sites to increase the water solubility (or hydrophilic character) of a surfactant. (Edwards et al., 1991).

Numerous batch and column studies have indicated that surfactants enhance recoveries of non-aqueous phase liquids (NAPLs) (Abdul et al., 1992; Kan et al., 1992; Soerens et al., 1992) by solubility enhancement or desorption. There have also been indications that pretreatment of a soil with surfactant washing (Igepal CA-720) to solubilize polycyclic aromatic hydrocarbons (PAHs) enhanced biodegradation of these contaminants (Joshi and Lee, 1995). The surfactant-aided remediation of ground water and washing of soil are technologies used to enhance the removal of organic contaminants (Abdul et al., 1992; Yeom et al., 1996), and cleaning of hydrophobic organic compounds (HOCs) from contaminated soil or sediment (Jafert et al., 1995; Chu et al., 1998; Chu and Chan, 2003). They are pretreatments to further degrade the surfactant/HOCs mixtures that are extracted from soils and sediments (Chu and Jafert, 1994; Chu, 1999). Surfactants are particularly attractive for this process as they potentially have low toxicity and favorable biodegradability; thus, they can be more environmentally friendly than many systems based on organic solvents. However, guidance in selecting the surfactants to be evaluated in the *ex situ* washing of soil is important for the soil remediation industry (Deshpande et al., 1999). The primary mechanism of enhanced aqueous solubility of organic contaminants is partitioning into surfactant micelles (Kile and Chiou, 1989), so surfactants have been proposed for use in soil washing and pump-and-treat technologies to assist the solubilization of sorbed hydrophobic contaminants by reducing surface and interfacial tension and by increase desorption. The removal of certain types of organic compounds from contaminated sites is handicapped by the very low solubilities of these compounds in water because of their nonpolarity and molecular sizes: the aqueous solubility of an organic contaminant decreases with decreasing polarity and increasing molecular size (Piwoni and Keeley, 1990). The water solubilities of such compound are greatly

enhanced by micellar solubilization if the aqueous phase contains a surfactant at a concentration above the critical micelle concentration (Clarke et al., 1991). The addition of organic solvent, besides the surfactant, may be inherent in the micellar core and further improve the soil-washing capability. On the other hand, the organic solvents were known as extra sources of electron donors, which is essential to the photodechlorination reaction (Chu and Choy, 2002).

Organic solvent refers to most other solvents that are organic compounds and contain carbon atoms. Solvents usually have a low boiling point and evaporate easily or can be removed by distillation, thereby leaving the dissolved substance behind. Solvents should therefore not react chemically with the dissolved compounds (they have to be inert). Solvents can also be used to extract soluble compounds from a mixture; the most common example is the brewing of coffee or tea with hot water. Solvents are usually clear and colorless liquids and most of them have a characteristic odor. The concentration of a solution is the amount of compound that is dissolved in a certain volume of solvent. The solubility is the maximal amount of compound that is soluble in a certain volume of solvent at a specified temperature (Reichardt, 1998).

Organic solvents and solutes can be broadly classified into *polar* (hydrophilic) and *non-polar* (lipophilic). The polarity can be measured as the dielectric constant or the dipole moment of a compound. The polarity of a solvent determines what type of compounds it is able to dissolve and with what other solvents or liquid compounds it is miscible. As a rule of thumb, polar solvents dissolve polar compounds best and non-polar solvents dissolve non-polar compounds best: "like dissolves like". A solvent will create various weak chemical interactions with the solute in order to solubilize it. The most common of these interactions are the relatively weak van der Waals interactions (induced dipole interactions), the stronger dipole-dipole

interactions, and the even stronger hydrogen bonds (interaction between O-H or N-H hydrogens with O or N atoms). Most organic solvents rapidly biodegrade in the soil or wastewater, i.e., they do not bioaccumulate or persist in the environment, and have relatively low ecotoxicity. However, many organic solvents are carcinogens (e.g., benzene, carbon tetrachloride, trichloroethylene), reproductive hazards (e.g., 2-ethoxyethanol, 2-methoxyethanol, methyl chloride), and neurotoxins (e.g., n-hexane, tetrachloroethylene, toluene). Solvent extraction uses an organic solvent, to remove metals and mixtures of metal and organic compounds. It is commonly used in combination with other technologies, such as solidification/stabilization, incineration, or soil washing. Soil is removed and treated. Solvent extraction has been shown to be effective in treating sediments, sludges, and soils containing primarily organic contaminants such as PCBs, VOCs, halogenated solvents, and petroleum wastes. This process has been shown to be applicable for the separation of the organic contaminants in paint wastes, synthetic rubber process wastes, coal tar wastes, drilling muds, wood-treating wastes, separation sludges, pesticide/insecticide wastes, and petroleum refinery oily wastes (Grasso et al., 1997). Properties of organic solvent and surfactant is shown in Table 2.1

**Table 2.1** Properties of organic solvent and surfactant

Organic solvent and surfactant	Chemical formula	Density (g.cm <sup>-3</sup> at 20°C)	Vapor Pressure (hPa at 20°C)	Boiling point (°C)	Molegular weight (g.mol <sup>-1</sup> )
Methanol	CH <sub>3</sub> OH	0.79	128	64.5	32.04
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	0.79	59	78.3	46.07

<i>n</i> -Butanol	$C_4H_{10}O$	0.81	6.7	116	74.12
<i>sec</i> -Butanol	$C_4H_{10}O$	0.81	16.5	100	74.12
<i>n</i> -Octanol	$CH_3(CH_2)_7OH$	0.83	0.031	195	130.23
Toluene	$C_6H_5CH_3$	0.87	29	110.6	92.14
Benzene	$C_6H_6$	0.88	101	80.1	78.11
Acetone	$C_3H_6O$	0.79	233	56.2	58.08
<i>n</i> -Hexane	$CH_3(CH_2)_4CH_3$	0.66	160	69	86.18
Triton X-100	$4-(C_8H_{17})C_6H_4(OCH_2CH_2)_nOH,$ $n \sim 10$	1.07	<0.01	>200	625
Tergitol NP-10	$C_9H_{19}C_6H_4O(CH_2CH_2O)_nH,$ $n \sim 11$	1.049	<0.01	>200	683
Tween80	$C_{24}H_{43}O_6(CH_2CH_2O)_{20}H$	1.07	<1.33	>100	1310
Brij35	$(C_2H_4O)_{23}C_{12}H_{26}O$	1.05	1.3	>100	1200
SDS	$CH_3(CH_2)_{11}OSO_3Na$	1.012	-	-	288

(Rosen, 1978; Reichardt, 1998)

### 2.2.4 Herbicide Photodegradation

Herbicide degradation ultimately ends with the formation of simple stable compounds, such as carbon dioxide; however, there are intermediates of varying stability on the way to complete mineralization (e.g.,  $H_2O$  and  $CO_2$ ). The rate of degradation of a particular herbicide can vary widely. The chemical nature of the herbicide is important but the degradation rate also depends on the availability of other reactants, as well as environmental factors.

Degradation of phenylurea herbicides in nature can be a relatively slow process because it is bio-recalcitrant and chemical stable. These pesticides can be decomposed by ultraviolet (UV) irradiation between 200-300 nm. Photodegradation is the breakdown of a herbicide by sunlight at the plant, soil, or water surface. Photodegradation of diuron by Photo-Fenton or  $\text{TiO}_2$  system have been recently studied with the aim of reducing diuron concentration in water (Malato et al., 2002). Total mineralisation (i.e., complete disappearance of total organic carbon, TOC) can be achieved after a long irradiation (more than 200 min). However, it appears that 90% of the initial TOC could be mineralized in approximately 125 and 159 min, respectively, with each technique, providing an interesting way to explore further in waste water treatment. In contrast the photodegradation of diuron under UV sunlight in natural seawater appeared very minor. This result could partially explain the reported quite long half-life of diuron from one month to one year (Okamura, 2002). Direct photolysis occurs when the herbicide absorbs light (some portion of the solar spectrum), and this leads to dissociation of some kind (e.g., bonds break). In indirect photolysis occurs when a sensitizer molecule is radiatively excited and is sufficiently long-lived to transfer energy, such as an electron, a hydrogen atom, or a photon to another "receptor" molecule. The receptor molecule (herbicide), without directly absorbing radiation, can be activated via the "sensitizer" molecule to undergo dissociation or other kinds of chemical reaction leading to photodegradation (Anderson and Schaeffer, 2004). There are four basic types of reaction in the photochemistry of the substituted phenylurea herbicides; they are photolysis of the -C-x bond on aromatics (x = Cl, Br), photoeliminations (Norrish-Type II reactions), photooxidations, and photorearrangements (Kotzias and Korte, 1981). The photocatalytic transformation of phenylurea herbicides leads to the formation of

several products. The structure of those resulting from (a) the attack of the hydroxy radicals on the aromatic ring and (b) abstraction of hydrogen atoms of the methyl group followed by the addition of oxygen and decarboxylation leading to the formation of dealkylated products. The distribution of products greatly depends on the pH of the medium. In neutral medium, the attack of the hydroxyl radicals is located both on the aromatic ring and on the methyl groups. In acidic medium, it is mainly located on the methyl groups, the hydroxylation of the aromatic ring being clearly unfavored with the decrease of the pH (Konstantinou and Albanis, 2003).

Titanium (IV) dioxide or titania ( $\text{TiO}_2$ ) is one of the most common metal-oxides recognized in many fields of application including the use as catalysts, catalyst supports, electronics, cosmetics, pigments and filler coating. Nevertheless, photocatalyst for pesticide destruction in water is one of the most important applications of titania for contaminated water remediation. Although titania is known to have three natural polymorphs, i.e. rutile, anatase, and brookite, only anatase is generally accepted to have significant photocatalytic activity (Nishimoto et al., 1985).

The primary step in the photocatalytic process involves the generation of excited species by the illumination of the  $\text{TiO}_2$  particle with light energy greater than the band gap energy. These species can either recombine or migrate to the surface of semiconductor, where several redox reactions may take place. The organic substrate reacts with the formed active species (oxidant or reducing) depending on its initial oxidation state and the nature of substituents, forming radicals and other species that are further oxidized or reduced (Konstantinou and Albanis, 2003).