

**NANOFILTRATION TREATMENT FOR PESTICIDES REMOVAL:  
A CASE STUDY FOR ATRAZINE AND DIMETHOATE**

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A CASE STUDY FOR ATRAZINE AND DIMETHOATE**

**by**

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## LIST OF SYMBOLS

|             |   | Unit   |
|-------------|---|--|
| $a$         | Osmotic constant                              | ( $\text{m}^3\text{Pa/g}$ )                      |
| $A$         | Membrane area                                 | ( $\text{m}^2$ )                                 |
| $C_{bs}$    | Solute bulk concentration                     | ( $\text{mg/L}$ )                                |
| $C_f$       | Pesticide concentration of feed               | ( $\text{mg/L}$ )                                |
| $C_p$       | Pesticide concentration of permeate           | ( $\text{mg/L}$ )                                |
| $C_s$       | Solute concentration in solution              | ( $\text{mol/m}^3$ )                             |
| $C_{ms}$    | Solute concentration at the wall of feed side | ( $\text{mg/L}$ )                                |
| $\bar{C}_s$ | Average solute concentration in solution      | ( $\text{mol/m}^3$ )                             |
| $dC_s$      | Solute concentration different in solution    | ( $\text{mol/m}^3$ )                             |
| $dP$        | Hydrostatic pressure driven different         | ( $\text{N/m}^2$ )                               |
| $dx$        | Axial direction difference                    | ( $\text{m}$ )                                   |
| $D_{sw}$    | Diffusion coefficient of solute in water      | ( $\text{m}^2/\text{s}$ )                        |
| $J_s$       | Solute flux                                   | ( $\text{mol/m}^2.\text{s}$ )                    |
| $J_v$       | Solvent fluxes                                | ( $\text{m/s}$ )                                 |
| $k_s$       | Mass transfer coefficient                     | ( $\text{m/s}$ )                                 |
| $K_{o/w}$   | Octanol/water partition coefficient           | (dimensionless)                                  |
| $L_p$       | Membrane permeability                         | ( $\text{m}^3/(\text{m}^2.\text{s}.\text{Pa})$ ) |
| $m$         | Solute molar mass                             | ( $\text{g/mol}$ )                               |
| $P_s$       | Solute permeability                           | ( $\text{mol/N.s}$ )                             |
| $P_s$       | Local solute permeability                     | ( $\text{m}^2/\text{s}$ )                        |
| $P_w$       | Hydrodynamic permeability                     | ( $\text{m}^3/\text{N.s}$ )                      |
| $\bar{P}_w$ | Specific hydraulic permeability               | ( $\text{m}^4/\text{N.s}$ )                      |

|                      |   |                                     |
|----------------------|---|-------------------------------------|
| $r_{sc}$             | Radius of stirred cell                      | (m)                                 |
| $R$                  | Percentage of pesticide rejection           | (%)                                 |
| $R^2$                | Coefficient of determination                | (dimensionless)                     |
| $R_{os}$             | Observed rejection                          | (dimensionless)                     |
| $R_s$                | True rejection                              | (dimensionless)                     |
| $R_g$                | Ideal gas constant                          | (m <sup>3</sup> Pa/mol.K)           |
| $Re$                 | Reynold number                              | (dimensionless)                     |
| $Sc$                 | Schmidt number                              | (dimensionless)                     |
| $Sh$                 | Sherwood number                             | (dimensionless)                     |
| $t$                  | Time  | (s)                                 |
| $T$                  | Operating temperature                       | (Kelvin)                            |
| $v_w$                | Permeate flux                               | (m <sup>3</sup> /m <sup>2</sup> .s) |
| $V$                  | Cumulative volume                           | (m <sup>3</sup> )                   |
| $x$                  | Vertical distance from the membrane surface | (m)                                 |
| <i>Greek letters</i> |   |                                     |
| $\sigma_s$           | Reflection coefficient                      | (dimensionless)                     |
| $d\pi$               | Osmotic pressure different                  | (N/m <sup>2</sup> )                 |
| $\Delta P$           | Hydrostatic pressure driven difference      | (N/m <sup>2</sup> )                 |
| $\delta$             | Concentration polarization layer thickness  | (m)                                 |
| $\rho$               | Density of solution                         | (kg/m <sup>3</sup> )                |
| $\omega$             | Stirring rate                               | (s <sup>-1</sup> )                  |
| $\Delta\pi$          | Osmotic pressure difference                 | (N/m <sup>2</sup> )                 |
| $\Delta t$           | Time difference                             | (s)                                 |
| $\mu$                | Viscosity of solution                       | (kg/m.s)                            |
| $\Delta V$           | Cumulative volume difference                | (m <sup>3</sup> )                   |

## LIST OF ABBREVIATION

|        |  |
|--------|--|
| AOP's  | Advanced oxidation processes                     |
| AChE   | Enzyme acetyl cholinesterase                     |
| ANOVA  | Analysis of variance                             |
| CFR    | Case fatality rate                               |
| CFSK   | Combined Film Theory-Spiegler-Kedem              |
| COD    | Chemical Oxygen Demand                           |
| CV     | Coefficient of variance                          |
| HPLC   | High Performance Liquid Chromatography           |
| IARC   | International Agency for Research on Cancer      |
| MCPA   | Malaysian CropLife and Public Health Association |
| MF     | Microfiltration                                  |
| NF     | Nanofiltration                                   |
| OZ     | Organo-zeolite                                   |
| PAC    | Powdered activated carbon                        |
| rpm    | Rotation per minute                              |
| RC     | Regenerated Cellulose                            |
| RO     | Reverse osmosis                                  |
| SK     | Spiegler-Kedem                                   |
| UF     | Ultrafiltration                                  |
| UK     | United Kingdom                                   |
| USA    | United States of America                         |
| UV/VIS | Ultraviolet-visible                              |
| WHO    | World Health Organization                        |



# **RAWATAN PENURASAN NANO UNTUK PENYINGKIRAN RACUN SERANGGA: KAJIAN KES BAGI ATRAZIN DAN DIMETOAT**

## **ABSTRAK**

Tesis ini memfokuskan kepada penyingkiran racun serangga dari larutan akues menggunakan membran penurasan nano. Dua jenis racun serangga, atrazin dan dimetoat, telah dipilih untuk diuji. Empat jenis membran penurasan nano (NF90, NF200, NF270 and DK) telah diuji dengan menjalankan penurasan hujung mati teraduk menggunakan larutan racun serangga. Melalui kajian ini, ia didapati bahawa NF90 menunjukkan prestasi penolakan yang terbaik, diikuti dengan NF200 dan DK. Sementara itu, walaupun NF270 menunjukkan prestasi hasil telapan yang tertinggi di antara empat membran yang diuji, ia menunjukkan prestasi penolakan yang paling lemah. Pada keseluruhannya, keempat-empat membran yang diuji dapat menolak atrazin dengan lebih baik daripada dimethoate secara konsisten.

Prestasi penolakan dapat ditingkatkan sebanyak lebih kurang 10% apabila penurasan dijalankan pada racun serangga yang dilarutkan dalam air paip atau air sungai. Pemantauan ini menunjukkan bahawa dalam kes sebenar di loji rawatan air, penolakan racun serangga yang lebih baik dapat dijangkakan. Akan tetapi, ini diperolehi dengan pengorbanan prestasi hasil telapan kerana hasil telapan yang lebih rendah dapat diperhatikan bagi penurasan air paip dan air sungai.

Prestasi penolakan dan hasil telapan didapati menunjukkan kesan positif apabila tekanan operasi dan kadar adukan ditingkatkan. Akan tetapi, ia dikenalpasti bahawa peningkatan kepekatan suapan racun serangga telah mengurangkan prestasi penolakan dan hasil telapan. Sementara itu, meningkatkan pH larutan telah menaikkan prestasi penolakan bagi NF200, NF270 dan DK. Walau bagaimanapun, prestasi hasil telapan menurun. Kes yang berlainan dapat dipantau bagi NF90 yang mana ia

menunjukkan prestasi yang konsisten tanpa mengira keadaan pH larutan. Pengaruh bahan larut perduaan atrazin-dimetoat terhadap proses penolakan juga dikaji dan ia dikenalpasti mengurangkan sedikit prestasi penolakan membran penurasan nano. Sungguhpun begitu, prestasi telapan tidak terpengaruh oleh sistem perduaan tersebut.

Keputusan ANOVA (analisis varians) daripada rekaan faktorial am menunjukkan bahawa secara amnya, kepekatan suapan racun serangga tidak memainkan peranan yang penting dalam prestasi penolakan dan hasil telapan racun serangga. Ia hanya didapati menunjukkan kesan yang ketara bagi prestasi penolakan atrazin. Faktor lain seperti jenis membran, tekanan operasi dan kadar adukan didapati memainkan peranan yang penting dalam prestasi penolakan dan hasil telapan racun serangga.

Pengesahan data eksperimen untuk membran dengan prestasi yang terbaik, NF90, menggunakan model Spiegler-Kedem telah menunjukkan penganggaran data eksperimen yang baik. Penentuan pekali ( $R^2$ ) yang diperolehi untuk pepadanan data adalah 0.9871 bagi atrazin dan 0.9692 bagi dimetoat.

# **NANOFILTRATION TREATMENT FOR PESTICIDES REMOVAL: A CASE STUDY FOR ATRAZINE AND DIMETHOATE**

## **ABSTRACT**

This thesis focuses on the removal of pesticide from aqueous solution using nanofiltration membrane. Two pesticides, atrazine and dimethoate, were selected for study in this research. Four nanofiltration membranes (NF90, NF200, NF270 and DK) were subjected to a stirred dead-end filtration of the pesticide solution. It was found that NF90 showed the best rejection performance, followed by NF200 and DK. Meanwhile, although NF270 showed the highest permeate flux out of the four membranes tested, it showed the poorest rejection. In overall, for the four membranes tested, atrazine was consistently better rejected than dimethoate.

The rejection performance was further enhanced by approximately 10% when filtration was done with the pesticide being dissolved in tap water or river water. This observation showed that in actual case of filtration in water treatment plant, better pesticide rejection performance could be expected. However, this was obtained at the expense of flux performance since lower permeate flux was observed for filtration of tap water and river water.

Increasing operating pressure and stirring rate posed positive effects on both rejection and flux performance of nanofiltration membranes. However, increasing the feed pesticide concentration reduced the rejection and flux performance. Increasing initial pH of solution increased the rejection performance of NF200, NF270 and DK. Nevertheless, this was accompanied with reduced permeate flux. Exceptional case was observed for NF90 whereby it showed somewhat consistent performance regardless of the initial pH of solution. The effect of atrazine-dimethoate binary solutes on the rejection was also studied and it was found that the presence of binary solutes

slightly reduced the rejection performance of the nanofiltration membranes. Nevertheless, the flux performance was observed not to be affected by the binary system.

ANOVA (analysis of variance) results from general factorial design showed that generally, feed pesticides concentration did not play significant roles in rejection and flux performance of pesticides in the system. It was found to be significant only in the case of rejection performance of atrazine. Other factors such as type of membrane, operating pressure and stirring rate were found to play significant role in the rejection and flux performance of pesticides.

Verification of experimental data for the best-performed membrane, NF90, using Spiegler-Kedem model showed that the model provided a good estimation of experimental data. The coefficient of determination ( $R^2$ ) obtained for the fitted data was 0.9871 and 0.9692 for atrazine and dimethoate, respectively.

# **CHAPTER 1**

## **INTRODUCTION**

### **1.0 Research Overview**

This chapter provides an overview of the research background. The scope covers from current scenario of pesticides usage in agriculture and how the pesticides found their way into the sources of drinking water. Then, the problem statement of this research is presented, followed by the objectives of this research as well as the scope of study and the organization of this thesis.

### **1.1 Pesticides in Agriculture Sector**

Malaysia is actively involved in agriculture practice, planting oil palm, paddy, fruit, vegetables and others for both local consumption and export purposes. In order to achieve the objectives such as to maintain the quantity and quality of agriculture productions, pesticides are used in agriculture sector as a mean of pest control for sustainability of the industry.

In Malaysia, the annual pesticides sales figure exceeds RM 300 million. It is estimated that annual crop losses in our country could exceed 30% without pesticides (MCPA, 2005). On the other hand, insects, weeds, fungi, viruses, parasites, birds and rodents consume or destroy approximately 48% of the world's annual food production (Yedla and Dikshit, 2005).

Crop losses could be translated into less food supply and subsequently resulted in surging of food price. It is inevitable that more pesticides will be utilized to cope with the demands by the increasing population as well as to fulfill the vision of our Prime

Minister, Datuk Seri Abdullah Ahmad Badawi, to transform agriculture sector into the main industry in Malaysia.

Malaysian CropLife and Public Health Association (MCPA) (2005) defined pesticide as chemical or a biological product developed and used for pests control. In agriculture, "pests" include insects, diseases, weeds and other organisms like nematodes which can have a devastating effect on the quality and quantity of crops harvested for food, grain and fibre.

Pesticides are also used in the public health sector to control vector borne diseases like malaria, dengue fever (both diseases spread by mosquitoes), river blindness disease (spread by snails), houseflies, cockroaches and termites that destroy building structures (MCPA, 2005). Ballantyne and Marrs (2004) stated that the word 'pesticides' is used to cover substances that control organisms (insects, fungi, plants, slugs, snails, weeds, micro-organism, nematodes, etc) which destroy plant life and interfere with food chain, and which act as vectors to disease organism to man and animals.

There are a variety of pesticides to be chosen from, be it fungicides, insecticides, herbicides, rodenticides, molluscides and nematocides. In Malaysia, there are over a thousand of pesticide products registered to Department of Agriculture (Department of Agriculture, 2005). It is estimated that about 70% of pesticides sold goes to the agriculture sector (MCPA, 2005).

## 1.2 Pesticides in Source of Drinking Water

In Malaysia, little attention has been given to the presence of pesticides in the source of drinking water and its adverse effects on human health. These huge amount of pesticides used are the emerging contaminants in drinking water supplies.

Overseas, public attention on the potential long-term consequences of pesticides on human health and environment has started since 1962 when Carson (1962) highlighted the matter in her book 'Silent Spring'. In year 2003, test done by a well-known non-government organization on Coca-Cola and Pepsi in India revealed the presence of unacceptably high levels of pesticide residue. In one sample of Coca-Cola, the presence of lindane, a carcinogen, was 140 times higher than the allowable limit (Kapoor, 2006). As for our country, the presence of pesticides was acknowledged by Tan *et al.* (1995) to be present in almost all the river systems in Peninsular Malaysia. In June 2005, it was reported in The Star newspaper (Jessy, 2005) that uncontrolled agricultural activities at Cameron Highlands had contaminated the rivers so acute that even drinking water from the treatment plants was polluted.

The effect of pesticides on the environment is very complex as undesirable transfers occur continually among different environmental sections. Pesticides that are sprayed in the air may eventually end up in soils or water. The atmosphere is an effective medium which can move airborne pesticides away from their application sites and redeposit them in far away locations (Majewski, 1991). On the other hand, pesticides applied directly to the soil may be washed off by rain into nearby bodies of surface water or percolate through the soil to lower soil layers and groundwater (Kamrin, 1997). Furthermore, it has been reported that pesticides metabolites have high potential of leaching in soil (Fava *et al.*, 2005). However, it was noted that the

movement of pesticide in and through the soil is primary a function of water solubility of the pesticides and of the adsorption capacities of the soil type (Lichtenstein, 1972).

Pesticides uses and transfers have already extended to urbanized catchments (Blanchoud *et al.*, 2004). As a matter of fact, contamination of drinking water by pesticides can occur through carelessness and nonagriculture uses as well such as accidental major spill, application in lawns and golf courses and back-siphoning (Gustafson, 1993). The following are potential sources of pesticides that can lead to drinking water contamination listed by Gustafson (1993):

- i) Application near surface water bodies
- ii) Spray drift during major application
- iii) Small intentional spills
- iv) Lawns and golf courses
- v) Agriculture drainage wells
- vi) Point sources at storage facilities
- vii) Poorly constructed wells
- viii) Glasshouses and nurseries
- ix) Abandoned wells
- x) Back-siphoning
- xi) Application near sinkholes

Beitz *et al.* (1994) has mapped out the multiple interaction between pesticides and ecosystem as shown in Figure 1.1. Meanwhile, Schnoor (1992) summarized the fate and transport of pesticides in the environment in Figure 1.2. The figures clearly show that pesticides would eventually end up becoming a possible threat to human's health via atmosphere and water. Low-level residues of pesticides in water generally may not present acute toxicity problems, but chronic effects will likely be of concern (Carsel and Smith, 1987). This is because pesticides could have chronic effects such



as cancer (Davies and Doon, 1987; Doull, 1989; Younes and Galal-Gorchev, 2000), Parkinson's disease (Cone, 2005), reproductive effects, fetal damage, delayed neurologic manifestations and possible immunologic disorders (Doull, 1989).

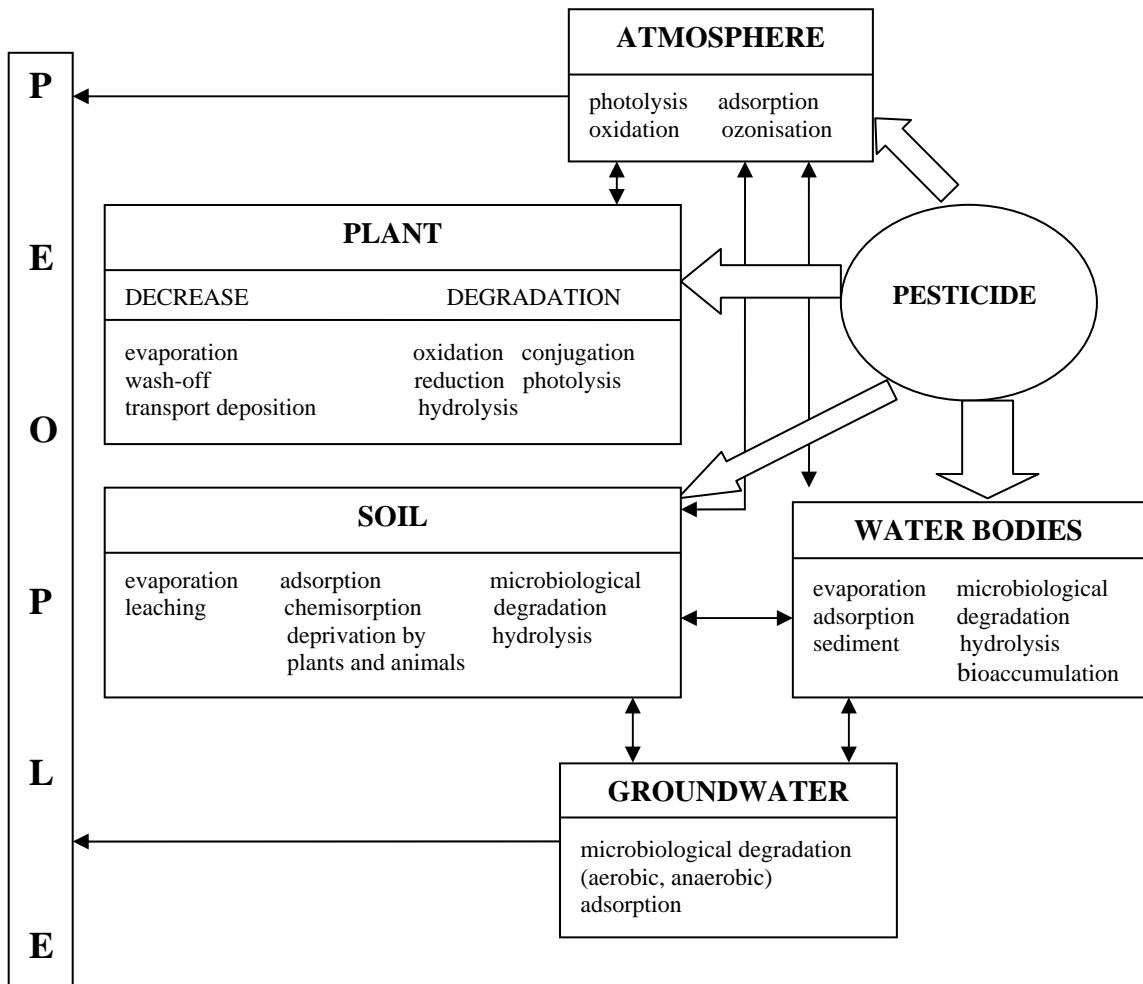


Figure 1.1: Interactions between pesticides and ecosystems (Beitz *et al.*, 1994).

### 1.3 Problem Statement

In 1987, World Health Organization estimated that up to 500,000 illnesses and as many as 20,000 deaths can be attributed annually to pesticidal chemicals worldwide (Wilkinson, 1987). Presently, on a worldwide basis, intoxications attributed to pesticides have been estimated to be as high as 3 million cases of acute and severe poisoning annually, with many unreported cases and with some 220 000 deaths (Kumazawa and Suzuki, 2000). This situation creates urgency to produce solution to remove pesticides

from the source of drinking water. This is because pesticides will continue to be effective pest controls, but it is up to us to find ways to avoid many of the pesticides poisonings and contaminations that exist today.

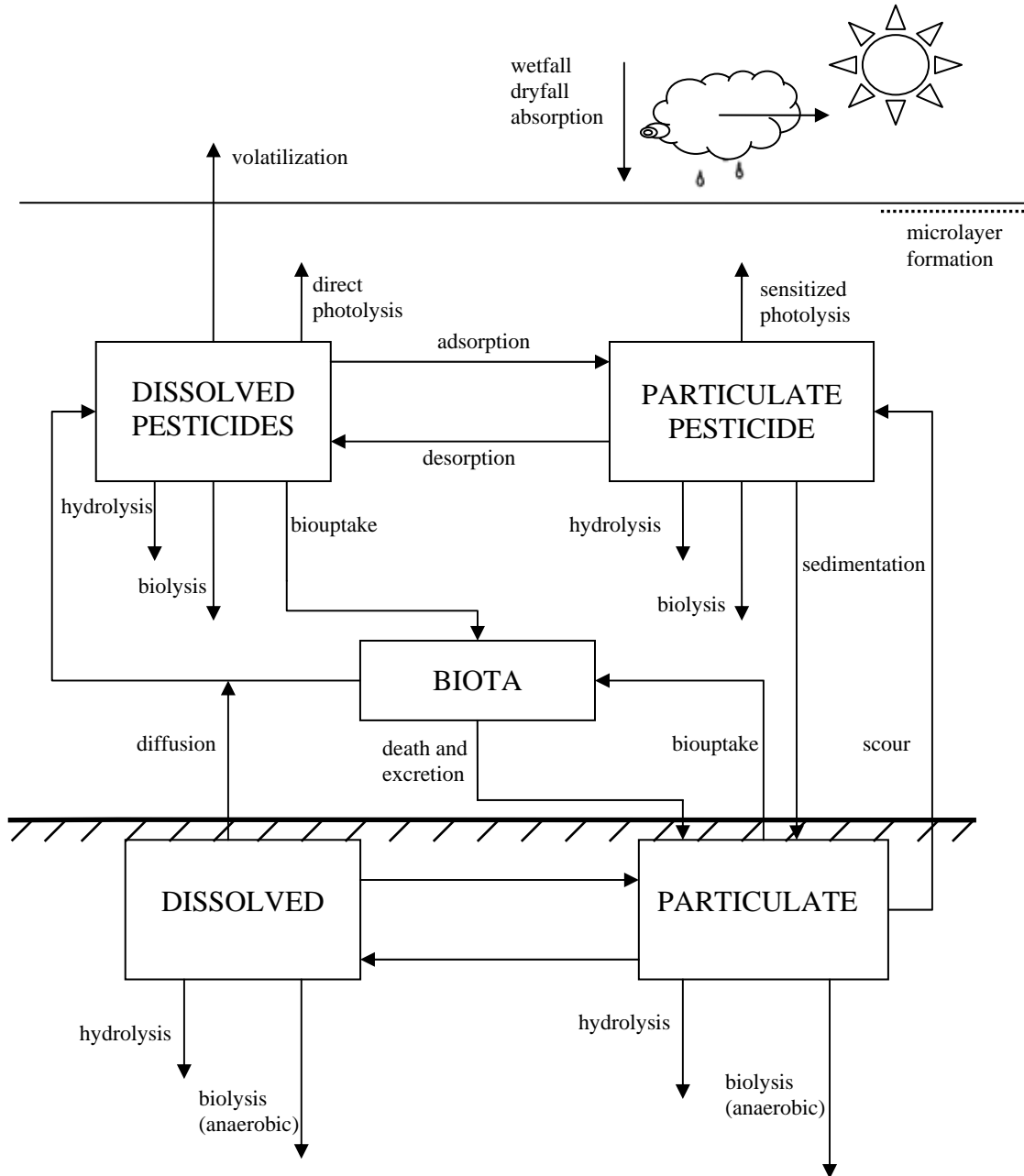


Figure 1.2: Pesticide fate and transport (Schnoor, 1992).

Traditionally, removal of pesticides for the production of drinking water is done by adsorption using activated carbon which is effective but requires frequent regeneration

(Van der Bruggen *et al.*, 1998). Besides that, chlorination, air stripping, coagulation, ozonation and advanced oxidation are also being used for treatment of pesticides from water (WHO, 2005). These methods however suffer from their own limitations and have limited successful applications in this area, leaving the vacuum to be filled by membrane technology. Although there could be fouling in membranes over the time, membrane processes are becoming increasingly widespread in water treatment applications due to its ability to achieve high removals of constituents such as dissolved solids, organic carbons, inorganic ions and organic compounds.

#### **1.4 Objectives of Research**

The objective of this research is to examine the performance of nanofiltration membranes in rejection of pesticides in aqueous solution. In order to achieve the main objective, the measurable objectives of this study are stated as follows:

- To evaluate the separation performance for different pesticides, different water quality and different commercial nanofiltration membranes in lab scale operation.
- To study the effect of experimental parameters namely operating pressure, pesticide concentration, stirring rate, pH of solution and binary solute mixture on rejection of pesticides and permeate flux.
- To investigate the significance of experimental variables such as membrane, operating pressure, pesticides concentration and stirring rate and on rejection of pesticides and permeate flux by applying general factorial design.
- To model the separation process and validate it using experimental data.

#### **1.5 Scope of Study**

This study focused on removal of atrazine and dimethoate from aqueous solution. Atrazine was selected as subject of study because this herbicide is commonly

used in the plantations around the world as well as in Malaysia (Chooi, 2005). Extensive amount of its usage has ranked it among the most common pesticides found in surface water and groundwater (Plakas *et al.*, 2006). On the other hand, dimethoate is also widely used in Malaysia and it is being regulated in guidelines for drinking water by World Health Organization. Nevertheless, data on effectiveness of dimethoate rejection using membranes has not been found so far (WHO, 2005).

Pesticides leaching would normally cause minute concentration of pesticides to be present in water and its chronic effect to the livings has been of more concern. Therefore, four polyamide nanofiltration membranes, NF90, NF200, NF270 and DK were examined for its performance in the pesticides rejection. Although the range of usual run-off case is in  $\mu\text{g/L}$ , the range of concentration used in this study is in  $\text{mg/L}$  as to consider in case of accidental spill of pesticides in water source.

A comparative study of atrazine and dimethoate rejection and permeate flux with NF90, NF200, NF270 and DK nanofiltration membranes was first conducted to gain initial insight of the performance of each membrane. Deionized water was used as solvent throughout the experimental works in order to get an accurate measurement of performance for pure pesticide concentration in water. However, a sub-section of this research was dedicated to investigating the membrane performance in different water quality. This would provide clearer understanding on nanofiltration performance in the real case of water filtration.

After that, a comprehensive study on the effect of experimental parameters towards the rejection and flux performance of atrazine and dimethoate with the nanofiltration membranes was carried out. Statistical tool was later applied to determine the significance of experimental variables. Finally, verification of

experimental data for the best-performed membrane was done by using Spiegler-Kedem model. This model was selected because unlike other models which are either only valid for reverse osmosis or inorganic molecules, this model has been acknowledged to be valid for retention of organic molecules in nanofiltration (Van der Bruggen and Vandecasteele, 2002).

## **1.6 Organization of the Thesis**

There are five chapters in this thesis. An overview on pesticides in agriculture sector and how pesticides could end up in source of drinking water are outlined in Chapter One.

Chapter Two presents a review of the literature. It is divided into five major sections. The first section gives a review about the current scenario of pesticides pollution in water. This is followed by explanation on pesticides which include their environmental fate and toxicology effect in section two. Detailed information on the pesticides chosen as subject of study, namely atrazine and dimethoate, is also presented in the section. Description on treatment technologies available for pesticides removal is provided in section three. Then, explanation on membrane filtration and nanofiltration process is given in section four. Section five focuses on the statistical approach used for factorial experimental design. A short summary on the literature review is presented in section six.

Chapter Three covers the methodology for the experimental work done in this research. This chapter is divided into six sections. The first section presents the materials such as membranes and chemicals used in the experiments. The second section gives a general description experimental set-up while the third section provides brief explanation on the analysis equipment used in this study. On the other hand, the

fourth section is a general description of the experimental procedures. The fifth section provides brief description on the statistical analysis approach chosen for this research while the final section gives explanation on how the modeling work was done.

Chapter Four presents all the acquired results and discusses on the findings. It is grouped into four main sections. Section one presents the results and discussion on the comparison of performances between the membranes tested by monitoring their performances when using pure water, pesticide solution in pure water and pesticide solution in different water quality. Section two examines the effect of operating conditions to the performances of the nanofiltration membranes while section three presents the statistical analysis done based on the general factorial design in order to investigate the significance of several main operating conditions to the performances of the nanofiltration membranes tested and interaction between the factors as well as the final regression model obtained from ANOVA. In section four, the performance of the best-performed membrane is validated using Spiegler-Kedem model.

Finally, Chapter Five gives the conclusion and some recommendations for future research. The conclusions are written according to the finding found in Chapter Four. Based on the conclusion, recommendations for future work are suggested.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.0 Introduction

This chapter provides the literature review of the pesticides pollution in water in section one. Section two provides an overview of history and chemical classification of pesticides as well as information regarding atrazine and dimethoate. After that, review of treatment technology available for pesticides removal is presented, followed by review on nanofiltration process. Literature review on statistical tools used to analyzed data is presented in section five and finally, a short summary on this chapter is provided in section six.

#### 2.1 Pesticide

Pesticide is a general term originated in the early days of its development. Initially, they were classified as contact poisons and stomach poisons. Later on, the classification was made based on their chemical composition and their application. Based on their application, pesticides can be classified into insecticides, acaricides, fungicides, bactericides, nematocides, rodenticides, molluscicides, weedicides, herbicides and soil fumigants. Until 1950's, insecticides were the major contributor of pesticides production. However, since 1954 when phenoxyacetic acid, a highly valuable herbicide, was discovered, the importance of weed control in protecting agricultural products was noticed. Since then, herbicides have been dominating the production as well as the market over insecticides (Yedla and Dikshit, 2005).

It was until 1962 when Rachel Carson's *Silent Spring* appeared that people were made aware of the hidden costs of pesticides and their potential in causing

adverse effects on human health and the environment (Wilkinson, 1987). Human can be exposed to pesticides either through skin, oral consumption or respiration (Ballantyne and Marrs, 2004). In order to provide a better picture of the types of pesticides available, their impact to environments as well as toxicology effect, Table 2.1 presents a general overview of several common groups of pesticides which are classified based on their chemical composition.

### **2.1.1 Atrazine**

Atrazine (2-chloro-4-(ethylamino)-6-isopropylamino-s-triazine) is a type of triazine herbicide (Kamrin, 1997). It was discovered in 1952 by scientists from J.R. Geigy Ltd. in Switzerland. Its first application was done in 1954 and it was patented in 1955 (Castelo-Grande *et al.*, 2005). Since then, atrazine has become the most widely used herbicide in agricultural and forestry applications, with 70,000–90,000 tonnes applied annually in the world. Atrazine has high effectiveness in inhibiting the growth of target weeds including variety of plants and some species of algae by interfering with the normal function of photosynthesis (Graymore *et al.*, 2001).

Herbicide contamination of water environment is of considerable concern because of the potential health hazard towards humans and animals, necessitating stringent legislation on the purity of drinking water. Coincidentally, being one of the most frequently applied herbicides in the agricultural sector, atrazine has frequently been detected in fresh water at levels exceeding the permissible limits (Chingombe *et al.*, 2006). This has led World Health Organization (WHO) to set guideline for drinking water and it allows a maximum of 0.002 mg/L of atrazine in drinking water (WHO, 2005). Figure 2.1 shows the molecular structure of atrazine.



Table 2.1: Chemical classification system of pesticide.

| Category                       | General information   | Environmental Impact   | Toxicology Effect   |
|--------------------------------|---|--|---|
| Carbamates<br>(Kamrin, 1997)   | <p>-Members of this family are effective as insecticides, herbicides and fungicides, although they are most commonly used as insecticides.</p> <p>-Work on both target and non-target species through inhibition of enzyme acetyl cholinesterase, a substance that transmit a nerve impulse from a nerve cell to a specific receptor such as another nerve cell or a muscle cell.</p>   | <p>-Generally are non persistent in the environment.</p> <p>-Degrade through chemical hydrolysis and microbial processes and are unlikely to bioaccumulate in aquatic systems.</p>   | <p>-Chronic exposure may cause adverse effects on organs or acetylcholinesterase levels.</p>  |
| ω<br>Organochlorine pesticides | <p>-Insecticides composed primarily of carbon, hydrogen, and chlorine (Coming Clean, 2006).</p> <p>-Powerful pesticides obtained at relatively low cost (Mitchell, 1966).</p> <p>-The compound's resistance to biochemical degradation, coupled with its solubility in fats (lipids), leads to bioaccumulation in living organisms. This has led to its banning or restriction for agriculture uses in many countries (Kamrin, 1997).</p> | <p>-According to Beitz <i>et al.</i> (1994), a pesticide is considered as high persistent in soil and water if its half-life is more than 1 month. Kamrin (1997) generalized that organochlorine pesticides possesses half-life between 2 to 10 years after it is applied to soil.</p> | <p>-May adversely affect fertility and reproduction at high doses and have carcinogenic effects at chronic exposure (Kamrin, 1997).</p> |

Table 2.1 Continued (a)

|                                     |   |   |   |
|-------------------------------------|---|---|---|
| Organophosphorus pesticides         | <p>-Inhibit the enzyme acetylcholinesterase (AChE) and thus over-stimulate neurological activity in organism (Pope, 1999).</p> <p>-Have higher toxicity than organochlorine pesticides, but are widely used in the world to replace the organochlorine pesticides due to its short half-life (Derache, 1977).</p> <p>-Due to the magnitude of their application, they are frequently associated with toxicity to animals and humans (Evgenidou <i>et al.</i>, 2005)</p> | <p>-Usually degrade within 2-4 weeks of application in soil (Ibrahim <i>et al.</i>, 1998).</p> <p>-Lakes and streams may be susceptible to pesticide runoff if application occurs prior to rainfall (Kamrin, 1997)</p>  | <p>-The commercial products are categorized from extremely toxic to moderately toxic. They are efficiently absorbed by inhalation, ingestion and skin penetration (Yusof <i>et al.</i>, 1995).</p> <p>-Although the degradation process usually leads to the formation of less harmful breakdown products, in some instances, it can produce more toxic products (Kamrin, 1997). Thus, the widespread uses of OPPs, coupled with the relative lack of reliable data on the risks of long-term exposure to human health have raised concern (Yusof <i>et al.</i>, 1995).</p> |
| Phenoxy and benzoic acid herbicides | <p>-One of the most controversial phenoxy compounds is 2,4,5-T. This compound was used extensively, together with 2,4-D, in the formulation of Agent Orange during the Vietnam War (Sahabat Alam Malaysia, 1984).</p> <p>- 2,4,5-T has been banned in Malaysia, but 2,4-D is still being sold (Department of Agriculture, 2005).</p>  | <p>-Most of the phenoxy and benzoic acid herbicides are of low persistence in soil, lasting up to 2 weeks.</p> <p>-However, despite the relatively rapid breakdown, they tend to be mobile in soil and thus, have the ability to move from soil into surface water or groundwater (Kamrin, 1997).</p> | <p>-Most phenoxy herbicides are moderately toxic while most benzoic acid herbicides are slightly toxic.</p> <p>-Phenoxy herbicides could cause liver and kidney damage as well as reproductive effects. Benzoic acid herbicides could have teratogenic effects at very high doses (Kamrin, 1997).</p>   |

Table 2.1 Continued (b)

|                                |   |   |  |
|--------------------------------|---|---|--|
| Phyrethroids<br>(Kamrin, 1997) | -Have biological origins.   | -Phyrethroids concentration decrease rapidly in pond waters and in laboratories degradation studies due to sorption, suspended particles and plants. Microbial and photodegradation can also occur. | -Categorized to be from slightly to moderately toxic.<br>-Exposure to high doses can be fatal<br>-Can cause liver effects.   |
| Triazine<br>(Kamrin, 1997)     | -Herbicides which consist of a single ring structure with three nitrogen atoms.<br>-Used against a wide variety of weed species by interfering with photosynthesis. | -Triazines do not adsorb to soil particles and may leach through soil.<br>-They are relatively stable in water (i.e. not easily hydrolyzed).  | -Triazine compounds are categorized from moderately toxic to slightly toxic.<br>-It could cause disruption of metabolism of vitamins, adverse reproductive effects and liver damage with high doses. |

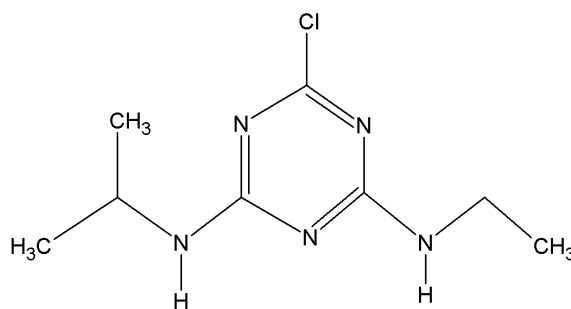


Figure 2.1: Structure of atrazine.

### 2.1.1(a) Environmental Impact

Atrazine is a common soil and water pollutant as atrazine applied to cropland can be transported to groundwater by infiltration or to surface waters by water runoff (Nélieu *et al.*, 2000; Barreiro *et al.*, 2007). This is because it has the properties of high leaching potential, persistence in soil, slow hydrolysis and low vapor pressure (Boyd, 2000). Atrazine also persists under cool, dry conditions, in a stable pH environment (Ta *et al.*, 2006).

Atrazine is soluble in water (28 mg/L, 20°C) and is moderately toxic to fish and highly toxic to aquatic invertebrates. It has half-life in soil and water of over 41 and 55 days, respectively (Perez *et al.*, 2006).

### 2.1.1(b) Toxicology Effect

Atrazine is a stable and low-biodegradable aromatic compound that can cause adverse effects on human health (Chu *et al.*, 2007). It can exhibit phenomena called biomagnification, which means it has the ability to concentrate in animal tissues as it moves up in the food chain (Castelo-Grande *et al.*, 2005).

Atrazine is classified as possibly carcinogenic by the IARC (International Agency for Research on Cancer) and is related to ovary cancer. The simultaneous intake of nitrate and atrazine holds the risk of formation of the strongly genotoxic *N*-

nitrosoatrazine. Chromosomal damage in human lymphocyst and an enhanced occurrence of non-Hogdkin's lymphoma were reported even at very low concentration of 0.1 µg/L *N*-nitrosoatrazine (Zhang *et al.*, 2004). Atrazine also has the power to increase the toxicity of arsenic in human cells (Gonzalez-Barreiro *et al.*, 2006).

### 2.1.2 Dimethoate

Dimethoate (O, O – dimethyl S – methylcarbamoylmethyl phosphorodithioate) is an organophosphorus insecticide with a contact and systemic action. It was introduced in 1956 (Fischer *et al.*, 1997). It is widely used against a broad range of insects and mites and is also used for indoor control of houseflies (Sharma *et al.*, 2005). Dimethoate exerts its neurotoxicity by phosphorylation of the enzyme acetyl cholinesterase (AChE) in the central and peripheral nervous systems (Sivapiriya *et al.*, 2006).

Dimethoate is a kind of high-effective pesticide that is extensively applied in agriculture. However, its residues have a negative effect on the environment and on the health of people because of its toxicity and stability (Zhang *et al.*, 2007). Therefore, dimethoate is listed as one of the chemicals from agriculture activities in which guideline value has been established. Its value in drinking water must be ensured to be below 0.006 mg/L (WHO, 2005). Figure 2.2 shows the chemical structure of dimethoate. It is an aliphatic derivative of organophosphorus pesticides.

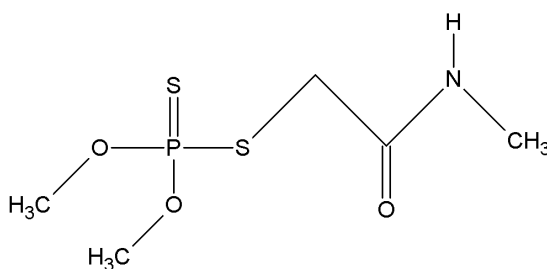


Figure 2.2: Structure of dimethoate.

### **2.1.2(a) Environmental Impact**

The acute and lethal effects of dimethoate have been determined in several aquatic invertebrate species. Acetyl cholinesterase (AChE) inhibition causes an accumulation of acetylcholine at nerve synapses and disruption of nerve function (Lundebyel *et al.*, 1997).

Dimethoate is highly soluble in water (25 g/L, 21°C) and it adsorbs poorly to any of the soils (Kamrin, 1997; Hernandez-Soriano *et al.*, 2006). Its high solubility in water has subjected it to considerable leaching as it can move rapidly through soils and end up in surface water or groundwater. It has half-life in soil and water of over 20 and 8 days, respectively (Kamrin, 1997).

### **2.1.2(b) Toxicology Effect**

Dimethoate is identified as moderately toxic compound in U.S. Environmental Protection Agency (Wilczek, 2005). . Dimethoate poisoning is usually associated with neuromuscular transmission block in both animals and humans (Sivapiriya *et al.*, 2006). Doull (1989) reported that dimethoate could cause mutagenicity, fetotoxicity and reproductive effects. Thyroid impairment can also occur due to its toxicity (Mahjoubi-Samet *et al.*, 2005).

Shahar *et al.* (2005) reported that a patient developed overt parkinsonism presenting with a resting tremor, expressionless face and lack of blinking along with marked cogwheel rigidity after an accidental ingestion of a raw eggplant sprayed with dimethoate. According to a survey on acute poisoning with pesticides in the state of Mato Grosso do Sul, Brazil, dimethoate was also associated with the highest case fatality rate (CFR) compared to other insecticides and herbicides (Recena *et al.*, 2006). In another study done on 802 patients with chlorpyrifos, dimethoate, or fenthion

poisoning admitted to three hospitals in Sri Lanka, the proportion of dying was significantly higher with dimethoate and dimethoate-poisoned patients died sooner than those ingesting other pesticides (Eddleston *et al.*, 2005).

More alarmingly, omethoate, the degradation product of dimethoate has been proven to be 10 times more toxic than its parent compound and it is more of a potential inhibitor to cholinesterase activity than dimethoate (Evgenidou, 2006). Moreover, the synergy effect of dimethoate-atrazine is more lethal than the effect of the individual pesticide since the toxicity of dimethoate was enhanced significantly when they are in binary combination (Anderson and Zhu, 2004).

## **2.2 Pesticides Pollution in Water**

Pesticide pollution in water may arise from runoff and leaching. Only a part of the applied amount of a pesticide is bioactive while the rest is distributed in the environment. Certain remaining amounts attached to the soil are leached out, migrate into groundwater or are distributed by surface runoff. A certain quantity reaches the air and can diffuse over long distances. The diagrams of pesticides cycle can be referred in Figure 1.1 and Figure 1.2.

Contamination of surface and ground waters by pesticides has been documented by several researchers in recent years. The findings are summarized in Table 2.2. In fact, accidents of pesticides' spills had been recorded in United States in 1969 and 1986. These two accidents were the cause for the development of chemical monitoring and acceleration of the sanitation programme and their implementation on the control of water quality (Van-Urk *et al.*, 1993).

Table 2.2: Summary of cases of pesticides contamination in water.

| Reference                            | Findings/Conclusions   |
|--------------------------------------|--|
| Gotz <i>et al.</i> (1998)            | Elevated amounts of some triazines pesticides and dimethoate were recorded in the River Elbe near Hamburg.   |
| El-Kabbany <i>et al.</i> (2000)      | The water monitoring study confirmed the presence of organophosphorus pesticides and carbamate pesticides in drainage water and canal water in El-Haram, Giza.   |
| Zhang <i>et al.</i> (2002)           | Total concentration for organophosphorus pesticides ranged from 134.8 to 354.6 ng/L and total concentration for organochlorine pesticides ranged from 115.4 to 414.7 ng/L was detected at Jiulong River Estuary, China.  |
| Gomez-Gutierrez <i>et al.</i> (2006) | Concentrations ranged from 0.4 to 19.5 ng/L for the organochlorine compounds and up to 170 ng/L for the more polar pesticides were found from the samples from the Ebro River, Spain.  |
| Guzzella <i>et al.</i> (2006)        | The results of the two-year monitoring campaign allowed to conclude that atrazine, even though it was banned in Italy in 1986, was still the main groundwater contaminant. It was present in 100% of the considered samples and 30% of them exceeded the allowable limit.  |
| Konstantinou <i>et al.</i> (2006)    | Pesticides which were mostly detected were herbicides, organophosphorus insecticides as well as the banned organochlorines insecticides due to their persistence in the aquatic environment. Rivers were found to be more polluted than lakes. The detected concentrations of most pesticides followed a seasonal variation, with maximum values occurring during the late spring and summer period followed by a decrease during winter. Nationwide, in many cases, the reported concentrations ranged in low ppb levels. However, elevated concentrations were recorded in areas of high pesticide use and intense agricultural practices. |
| Lapworth and Goody (2006)            | Diuron was observed in 90% of groundwaters sampled between year 2003 and 2004. Longer-term (1989-2005) monitoring showed that pollution of the aquifer by atrazine, simazine, and more recently diuron, shows a positive correlation with periods of high groundwater levels.  |



Table 2.2 Continued.

|                                |   |
|--------------------------------|---|
| Morvan <i>et al.</i> (2006)    | Five years after the ending of atrazine application which was used since the sixties, atrazine and its degradation product, deethylatrazine were still systematically quantified at the outlet of the watershed with concentrations from 0.07 to 0.43 µg/L for atrazine, and between 0.14 and 1.16 µg/L for deethylatrazine.  |
| Blanchoud <i>et al.</i> (2007) | The obtained data showed a similar contribution by urban pesticides in the Marne River, France due to runoff over impervious surfaces as compared to agricultural pesticides used on cultivated soils (about 11 tons/year in both cases).   |
| Moore <i>et al.</i> (2007)     | Both surface water and sediment phases of the three Mississippi Delta oxbow lakes examined had greater levels of current-use pesticide contamination than other previously studied watersheds due to more intensive cultivation and the concomitantly greater amounts of pesticide run-off from adjacent agricultural fields. |

The implementation on the control of water quality is important because different type of pesticides have different decaying period. Pesticides such as organophosphorus pesticides have half-life between several weeks to a few months while organochlorine pesticides can accumulate in the environment and in livings for years. The persistence and fate of pesticides is also dependent to a multitude of environmental factors such as soil types, temperature, light, moisture, microorganism, etc. It is for these reasons that no absolute half-life can be attributed to any pesticides (Lichtenstein, 1972). A study by Halimah *et al.* (2005) showed that a double increment from recommended pesticides dosage increases the day of detection after treatment from one day to five days. In a study carried out in Mississippi soybean fields, it was found that the downstream of the Yazoo River was contaminated with methaxychlor and endosulfan even after 3 weeks and 3.5 km far from the application site (Yedla and Dikshit, 2005).

During runoff events, residues of pesticides find way into coastal waters, rivers, estuaries and mangroves and were reported to be responsible for many massive fish kills (Yedla and Dikshit, 2005). Even after degradation, the breakdown products of pesticides can be less, more or similar in toxicity when compared to the parent chemical. This scenario inadvertently affects the aquatic livings by enhancing or decreasing populations, inhibiting or stimulating respiration or inhibiting the growth of the aquatic livings (Sumasundaram and Coats, 1990). If this situation is left unattended, it will eventually lead to ecological chaos. Besides, more humans are falling victim to the man-made poisons (Sahabat Alam Malaysia, 1984). In view of this unhealthy scenario, more attention has been given by regulatory bodies to monitor the water quality from pesticides contamination.

In Malaysia, no specific local water regulation on pesticides content has been implemented by government so far. However, there is a provision for the regulation of import, manufacture and sales of pesticides which exists under the Pesticides Act 1974 (amended in 2004). Its objective is to ensure that pesticides imported, manufactured and sold in the country are of good quality and that they will not cause adverse effects on man, food crops and the environment (Department of Agriculture, 2006). This outline of objective is still very wide, general and vague. Nevertheless, according to the Drinking Water Quality Standards in Malaysia, the content of certain pesticides in drinking water is monitored up to four times a year by referring to the limit set by World Health Organization (WHO) (Perbadanan Bekalan Air Pulau Pinang, 2007).

### **2.3 Treatment Technologies for Pesticides Removal**

Unlike heavy metals and other pollutants, pesticides are lethal to the environment even at micro level of concentrations (Yedla and Dikshit, 2005). The conventional water treatment processes such as alum coagulation, clarification and chlorination had been concluded to produce insignificant pesticides removal (Sisodia *et*

*al.*, 1996). This situation was also demonstrated at the A.H. Weeks drinking water treatment plant at Ontario, Canada, whereby sand filtration and flocculation by aluminum sulfate were proven ineffective in removing trace levels of atrazine (Hua *et al.*, 2006). Hence, in order to protect the environment and to meet the stringent enforcement regulations, many researchers are competing to produce effective, reliable and economical way for pesticide-containing water treatment system.

Current treatment technologies for pesticides treatment can be divided into three categories. They are chemical, physical and biological methods. Chemical treatment using advanced oxidation processes (AOP's) has gained interest of researchers lately due to its ability to destruct organic compounds. Biological method is still in its infancy in this area and it is still facing many challenges that needed to be overcome. On the other hand, physical treatment such as adsorption and membrane filtration has produced satisfactory results in removing pesticides from water. Table 2.3 summarizes the available methods for pesticides removal and findings by researchers.

## **2.4 Membrane Filtration**

Membrane is a barrier which separates two phases and restricts the transport of various chemical species (Strathmann, 1990). Microfiltration, ultrafiltration and reverse osmosis are among the well established membrane separation processes. Ultrafiltration and microfiltration are basically similar in their mode of separation. They separate by molecular sieving through increasingly fine pores. However, in reverse osmosis membranes, the membrane pores are so small that solutes permeate the membrane by dissolving in the membrane material and diffusing down on a concentration gradient. Separation occurs because of the differences in solubilities and mobilities of different solutes in the membrane (Baker, 2004). Nanofiltration is the most recently developed pressure-driven membrane separation process and has properties that lie between those of ultrafiltration and reverse osmosis (Oatleya *et al.*, 2005).

Table 2.3: Treatment methods available for pesticides removal and findings by researchers.

| Treatment methods                    | Findings/Conclusions   | References  |
|--------------------------------------|--|---|
| Advanced oxidation processes (AOP's) | <ul style="list-style-type: none"> <li>-Based on the production of hydroxyl radicals as oxidizing agents to mineralize synthetic organic chemicals.</li> <li>-These radicals are the second strongest oxidative species after fluorine (reduction potential <math>E_0 = 2.8</math> V) and they attack unselectively most of the organic molecules, resulting in a partial or total decomposition.</li> <li>- The commonly applied AOP's are ozonation, Fenton's process and photocatalytic oxidation.</li> </ul>   | Evgenidou <i>et al.</i> (2005)  |
| (a) Ozonation                        | <ul style="list-style-type: none"> <li>-Decrease of 66–96% of the atrazine concentrations was observed when ozone treatment was integrated in the A.H. Weeks drinking water treatment plant which serves the City of Windsor, Ontario Canada.</li> <li>-Complete degradation of a mixture of several pesticides (alachlor, atrazine, chlorfenvinphos, diuron and isoproturon) in aqueous solutions at pilot-plant scale was found to be slow.</li> <li>-It was also hard to accomplish as large amounts of the oxidant were required to lower the organic content of the solutions.</li> </ul>   | <p>Hua <i>et al.</i> (2006)</p> <p>Maldonado <i>et al.</i> (2006)</p>       |
| (b) Fenton's process                 | <ul style="list-style-type: none"> <li>-Studied on the oxidation of atrazine in the presence of hydrogen peroxide (<math>H_2O_2</math>) and ferrihydrite at different concentrations and pHs.</li> <li>-The decomposition product of atrazine was detected only after 1 day of experiment and a decrease of atrazine by 21% was observed over a period of 8 days.</li> </ul>   | Barreiro <i>et al.</i> (2007)   |
| (c) Photocatalytic oxidation         | <ul style="list-style-type: none"> <li>-Studied on photocatalytic oxidation of azynphos-methyl and dimethoate in water.</li> <li>-It was found that <math>TiO_2</math> absorbed light only in the narrow UV range of the solar spectrum, therefore, <math>FeCl_3</math>, another photocatalyst and also, probably, photosensitizer for <math>TiO_2</math>, must be used.</li> <li>-Concluded that solar light can be used together with small amount of <math>FeCl_3</math> and <math>TiO_2</math> for a tertiary treatment to eliminate pollutant as pesticides in a short time as the decomposition took place at higher rates compared to photocatalytic oxidation by using only either of them.</li> <li>-<math>TiO_2</math> was a more efficient photocatalyst compared to <math>ZnO</math> since the oxidation and decomposition of dimethoate proceeded at higher reaction rates.</li> <li>-However, complete mineralization was not achieved in both systems and the authors proposed longer irradiation time or higher quantities of the catalysts for better performance.</li> </ul> | <p>Dominguez <i>et al.</i> (1998)</p> <p>Evgenidou <i>et al.</i> (2005)</p> |