INVESTIGATION OF HERBICIDE SORPTION IN SOILS OF RICE FIELDS IN SEBERANG PERAK AREA

by

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CERTIFICATION OF APPROVAL

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Approved by,

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(AP Dr Amirhossein
Malakahmad)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
SEPT 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(MUHAMMAD AZZAM BIN RAZALI)

ABSTRACT

Clearfield® Production Systems (CPS) had been introduced in Malaysia to effectively control weeds in paddy fields area in Malaysia, which consisted of Imidazolinone tolerant rice (IMI-TR) seeds and On Duty® herbicides (an Imidazolinone herbicide mixture of imazapic and imazapyr). However, due to their high soil persistence imazapic and imazapyr herbicides can contaminate the environment and result in damages to rotational crops and non-target aquatic plants. Soil sorption can affects the herbicidal activity and soil persistence. So, the objective of this study is to investigate the adsorption and desorption in soils of paddy field. The soil samples were taken from paddy field area in Seberang Perak area and labeled 322, 328, 327 and X–mining soil. With reference to the researches done previously, a few soil properties had been selected which are related to the adsorption and desorption process. The properties are soil pH, total organic carbon, clay content, maximum water holding capacity, field capacity and cation exchange capacity(CEC). The adsorption study was done using batch equlibration method while the desorption study was done using single-step decant-refill technique. The adsorption and desorption data obtained were fitted with the Freundlich sorption isotherm. For adsorption, the R2 value was in the range of 0.985 to 0.997 with 1/n ads value was less than 1 which indicated the isotherm was non-linear. For desorption, the R2 value was in the range of 0.906 to 1 and hysteresis coefficient,H ranging from 1.19 to 2.80. The adsorption process was much affected by soil pH, maximum water holding capacity and field capacity while the desorption process was much affected by CEC and clay content. The adsorption rate was negatively correlated to soil pH, maximum water holding capacity. In addition, the desorption rate was positively correlated with CEC and clay content. The finding of this study provides useful information to reduce the environmental contamination of On Duty® herbicides in paddy fields area.

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Muhammad Azzam Razali

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CHAPTER 1
INTRODUCTION

1.1 BACKGROUND OF STUDY

Rice is one of the main economy resources for Malaysia. Many farmers especially in rural areas work out the paddy field as their main source of income. However recently the rice yield has experiencing some loss of production due to the presence of pest such as weeds. In order to control these weeds, the most trusted method that has been developed nowadays is the application of herbicides. Although the herbicide usage does increase the production cost of the farmer, but it is proven to be very effective to kill and control the weeds especially *Oryza sativa* complex species. In Malaysia, Federal Land Consolidation and Rehabilitation Authority (FELCRA) had introduced a system called Clearfield$^{®}$ Production Systems (CPS) combines bred herbicide-tolerant crops with herbicides to control weeds. Currently, CPS is applied with the imidazolinone-tolerant rice (IMI-TR) to control weeds especially weedy rice. Farmers are supplied with On Duty® herbicides (a mixture of imazapic and imazapyr) herbicide that when sprayed, would kill all weedy rice but not the IMI-TR, which are resistant to the herbicide. The IMI-TR seeds and On Duty® herbicides are sold together as a package.This package is offered to farmers as an alternative to kill the pest and at the same time it is accepted as common approach for the farmers to apply (Azmi et. al., 2012).

According to Azmi et. al. (2012) farmers can gain as many profits as possible by using the On Duty® herbicides. It decreases the production costs and herbicide usage volume. It also allows good timing flexibility in herbicide application and saves water through delayed flooding.

1.2 PROBLEM STATEMENT

However, the use of herbicides in paddy fields nowadays is becoming a major concern in environmental aspects. Due to the herbicides are highly effective for pest management, farmers become eager to use it frequently and it leads the herbicides to be overused and misused. There is concern in the usage of herbicide in a land cultivated with multiple crops in a year (Sudianto et al., 2013). This condition is quite similar to Malaysian tropical condition where rice is cultivated 2 to 3 times in a year.The residual activity of On Duty® herbicides can potentially injure the rotational crops (Sudianto et al., 2013). Thus, it will potentially affect the rice yield for the rotational rice cultivation.

Besides, Martini (2013) shows that that these herbicides have contaminated the surface and ground water in the certain agriculture areas. This is an important research area to be concerned since rice is considered as one the main economy resource in Malaysia. This environmental problem has attracted researches to come out more efficient and environmentally-friendly ideas to solve the weeds problem in paddy fields. Contamination of surface and ground water sources by herbicide is believed to be related to the high soil persistence and water solubility of the On Duty® herbicide that can increase their mobility in the environment (Martini et al., 2013). In Malaysia, the tropical climate condition seems unsuitable since the rain occurrence is quite heavy and frequent in number. This climatic condition believes to assist the mobility of the On Duty® herbicide used to the water sources. Although On Duty® herbicides are not toxic to human and animals but it can still harm the other plant.

The soil sorption process can reduce the mobility of herbicides in environment (Sun et al., 2012). Sorption process is related to the adsorption and desorption of the herbicide to the soil. Thus, the study of the adsorption and desorption properties of soils is very important to solve this problem. Different soils having different characteristics represent different adsorption and desorption properties. The study of these differences and the effective factors are necessary to protect the environment against the On Duty® herbicides contaminations.

1.3 OBJECTIVES

The objectives of this study are as follows:

1) To investigate the adsorption and desorption of Imazapyr in paddy soil.

CHAPTER 2

LITERITURE REVIEW

2.1 OVERVIEW OF THE STUDY

Rice is one of the important parts in Malaysian diet. It is one of the staple food consume by the Malaysian. Recently, the rice production within the country is less than the rice consumption of Malaysian. It is estimated that the rice yield of the country is only 80% compare to rice required. This situation leads the government to import rice from the other country in Southeast Asia region such as Vietnam, Pakistan, India, Myanmar and Thailand. This rice import activity does involve higher cost (Omar,2008).

Besides, the rice produced also experiencing some loss due to many affecting factors. This lead to the rice yield production to decline quantitatively. Hence, the government encourages the farmers to implement any reasonable initiative to increase the rice production.

Based on some research done by Rice and Industrial Crop Research Centre, Malaysia Agricultural and Development Institute (MARDI), there are some factors affecting the low yield of rice by the farmers. One of the significant factors is the presence of weeds. Weeds are plants that grow in a place that it is undesirable and interferes the activities there (Zimdahl, 2007).

According to Andres (2013), in Brazil, the main weeds in flooded rice fields are commonly classified into narrow- and broad-leaved weeds. The major representatives of narrow leaves are weedy rice (*Oryza sativa*), barnyardgrass (*Echinochloa* sp.), the aquatic grasses (*Leersia hexandra* and *Luziola peruviana*), and the sedges (*Cyperus difformis*, *C. esculentus*, *C. ferax*, and *C. laetus*). There was also an increase in the occurrence of monocotyledonous weeds such as Alexander grass (*Brachiaria plantaginea*), crabgrass (*Digitaria horizontalis*) and goosegrass (*Eleusine indica*) in the rice fields due to the increase in crop diversification in lowland areas, to the continued use of ALS inhibitors and the abandonment of propanil herbicide in the rice fields. There are also reported the presence of perennial weeds such as Olive hymenachne

(*Hymenachne amplexicaulis*), ribbed murainagrass (*Ischaemum rugosum*), Mexican sprangletop (*Leptochloa uninervia*), fall panicum (*Panicum dichotomiflorum*), Knotgrass (*Paspalum distichum*) and *Paspalum modestum* in some places with excess of moisture.

As broadleaved weed representatives, there are the jointvetches (*Aeschynomene* spp.) ,some species of morning glory (*Ipomoea* spp.), water pepper (*Polygonum hydropiperoides*) and alligator weed (*Alternanthera philoxeroides*). The examples of the aquatic weeds present in water seeded system fields are globe fringerush (*Fimbristylis miliacea*), arrowheads (*Sagittaria montevidensis* and *S. guyanensis*), water hyacinth (*Eichornia crassipes*), kidneyleaf mudplantain (*Heteranthera reniformis*) and the Ludwigia complex (*Ludwigia elegans*, *L. longifolia* and *L. octovalvis*). In addition, there are some species of the weeds have acquired resistance to herbicides. These weeds could not be controlled by the herbicide. The examples of the herbicide-resistant weeds are as the following Table:

The growth of weeds such as weedy rice will increase production cost. Due to that increment, farmer’s income will be reduced quantitatively through yield reduction and qualitatively through lower rice value at harvest. It was reported that in Asia, rice yield losses due to weedy rice infestation was around 16% to 74%. To be specific, in Malaysia, a yield loss of about 1 ton per hectare by the infestations of 35 weedy rice panicles per meter area (Chauhan, 2013). It was such a big loss occurs to the rice crop production.

According to Chauhan(2013), the widespread occurrence of weedy rice in Malaysia are favoured by direct seeding rice culture implementation, the use of easy shattering cultivars, and the use of combine harvesters. Moreover, the population growth rate of weedy rice are determine by weedy rice seed remain dormant in the soil over long time, weedy rice seed spread through crop seed contamination, and weedy rice seed from plants in the previous rice crop. Naturally, weeds have rapid seedling growth and good environmental plasticity. The weeds can increase their population very fast compared to the crop and they are capable of growing in wide range of climatic and edaphic conditions. The weeds will competite with the crops in the fields for nutrients, water and light. This can cause harmful effects to the crop production. **Table 2.1** shows the herbicide-resistant weeds reported in irrigated rice in Southern Brazil.

Table 2.1: Herbicide-resistant weeds reported in irrigated rice in Southern Brazil.

SPECIES	COMMON NAME	ACTIVE INGREDIENT CONFIRMED
Sagittaria montevidensis	arrowhead	Azimsulfuron, bentazon, bispyribac-sodium, cyclosulfamuron, ethoxysulfuron, imazapic+imazethapyr, metsulfuron, penoxsulam, pyrazosulfuron-ethyl
Echinochloa spp.	barnyardgrass	Quinclorac, Bispyribac-sodium, flucarbazone, imazapyr, imazethapyr, imazethapyr+imazapic, imazapyr+imazapic, nicosulfuron, penoxsulam, quinclorac
Cyperus difformis	nutsedges	Azimsulfuron, bispyribac-sodium, cyclosulfamuron, ethoxysulfuron, penoxsulam, pyrazosulfuron-ethyl
Cyperus iria	nutsedges	Bispiribac-sodium, Ethoxysulfuron, imazapyr+imazapic, imazethapyr+imazapic, penoxsulam, pyrazosulfuron-ethyl
Fimbristylis miliacea	globe fringerush	Azimsulfuron, bispyribac-sodium, cyclosulfamuron, ethoxysulfuron, penoxsulam, pyrazosulfuron-ethyl
Oryza sativa	weedy rice	Imazethayr +Imazapic Imazapyr

2.2 SOLUTION FOR WEEDS PROBLEM

This weeds problem will be more critical if no action is taken. These problem can be catered using many methods whether by preventive, cultural, mechanical, biological or chemical methods. Currently, the most economical, effective and convenient way to solve the weed problem is the implementation of chemical method by using herbicides.

So, for weeds , most of the farmers used herbicide to control weeds population. According to Norton et.al (2010), herbicides have long been the main weed management method for rice in Latin America, North America, Japan, Republic of Korea, and they are an important intervention in other Asian countries such as Sri Lanka and Vietnam. The herbicide used will kill, weaken, or suppress the weeds (Bajwa, 2014). Operationally, the fields may be sprayed with an herbicide that is toxic to the weeds, but not to the crop species. Consequently, the pest plants are selectively eliminated, the growth of the desired plant species is maintained (Zanella, 2011).

Herbicide usage is considered as cost effective compare to mechanical and cultural method which needs more time and energy to perform them. The application of herbicide also can set the paddy field to have earlier planting dates, have less tillage and most importantly farmers can have more time to perform other important daily life activities. Capri and Karpouzas (2008) estimated that without the application of herbicides, about 90 percent of rice production will be lost.

Herbicide does have their own suitability to be implemented in the field area. Generally, the concept is that different crops and field do need different herbicide to be used. Each herbicide has different chemical properties and herbicidal activity to each other. Bajwa (2014) stated that herbicides are available depending upon their mode of action, chemical composition, formulation, selectiveness and efficacy.

The selection of herbicide can be made based on the mode of action which means the works of the herbicide to kill the weeds. By understanding the mode of action, later, some other important matters can be determined such as which group of weeds is killed, application techniques specification, herbicide injury problems diagnostic and herbicide resistant weeds prevention. The application of the herbicide really gives some benefits to the farmers. According to Zimdahl (2007) , the advantages of using herbicide are as follow:

- Save labor and energy with reduction of hand labor and mechanical tillage;
- Reduce the needs of fertilizer and irrigation requirement due to competing weeds elimination;
- Reduce harvest costs due to elimination of interfering weeds;
- Reduce grain drying costs due to absentees of green and weedy plant material;
- More efficient method to control the weeds.

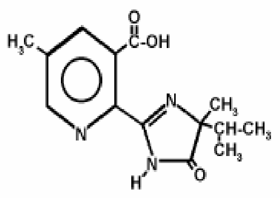
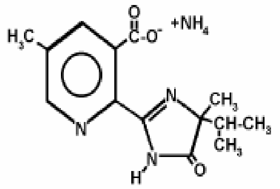
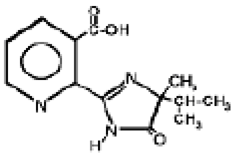
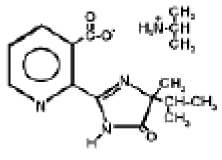
Furthermore, Chauhan (2014) stated that herbicide-resistant rice cultivarts is consider one of the option to manage weedy rice problem in Asia. Currently, there are three kinds of herbicide resistant rice: imidazolinone-, glyphosate-, and glufosinate-resistant rice. Imidazolinone herbicides can control a broad range of weeds and they have a residual effect, while, glyphosate and glufosinate can kill a broad range of weed flora, which would permit less herbicide use in terms of amount and number of applications. Both of these non-selective herbicides are applied as post-emergence. Their doses can be adjusted according to the weed infestation and the spraying window can be wider. All of these herbicides share some important characteristics such as broad spectrum control of weeds, long-term weed control, flexibility in crop rotation, biodegradable in nature, and effectiveness at low doses, thus reducing the total amount of herbicide released in the environment. In addition, weeds resistant to currently used herbicides could be controlled with these broad-spectrum herbicides. In 2010, two imidazolinone resistant rice (Clearfield) cultivars were released in Malaysia in 2010 to reduce weedy rice infestation. In other Asian countries, herbicide resistant rice has not been commercialized yet.

The introduction of these two Imidazolinone resistant rice was under the application of Clearfield Production System (CPS). CPS had been introduced to about seven granary areas in Malaysia which are Kedah, Perlis, Terengganu, Kelantan, Perak, Selangor and Penang, with satisfying outcome when the yields from CPS fields had doubled from 3.5

metric tons/ha to 7 metric tons/ha (Sudianto et al., 2013). Main components of this system are the combination of imidazolinone tolerant varieties (IMI-TR) and imidazolinone herbicides (Azmi et. al, 2012). Imazapic and Imazapyr are the imidazolinone herbicides use in CPS in rice fields of Malaysia (Tu et.al, 2001). The characteristics of each herbicide are shown in **Table 2.2**.

Table 2.2: The properties of imazapyr and imazapic herbicides.

CHARACTERISTICS	HERBICIDE	
	IMAZAPIC	IMAZAPYR
CHEMICAL FORMULA	(±)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1Himidazol-2-yl]-5-methyl-3-pyridinecarboxylic acid	(+)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-pyridinecarboxylic acid
HERBICIDE FAMILY	Imidazolinone	
TARGET SPECIES	selected annual and perennial broadleaves and grasses	grasses, broadleaves, vines, brambles, shrubs and trees, riparian and emerged aquatics
FORMS	acid, ammonium salt	acid & salt
FORMULATIONS	SL, DG	SL, GR
MODE OF ACTION	Inhibits the enzyme acetohydroxyacid synthase (AHAS), that is involved in	Amino acid synthesis inhibitor

	the synthesis of aliphatic amino acids	
WATER SOLUBILITY	2200 mg/L at 25° C	11,272 ppm
ADSORPTION POTENTIAL	low	
PRIMARY DEGRADATION MECHANISM	microbial activity	Slow microbial metabolism and photolysis
MOBILITY POTENTIAL	low	high
CHEMICAL BOND	 Imazapic acid  Imazapic ammonium salt	 Imazapyr acid  Imazapyr isopropylamine salt

The CPS system is able to control the weedy rice problem effectively (Azmi, 2012). CPS system had been used by many other countries such as U.S., Brazil, Colombia, Costa Rica, Italy and Uruguay (Sudianto et al., 2013). Kleemann (2009) reported that imazapic and imazapyr have been used in controlling the weeds growth. Both imidazolinone-typed pesticides proved to effectively control the rigid brome in wheat in Southern Australia. The effectiveness percentage was proved to be greater than 87 percent.In general, Imidazolinone has been used at low dosage to control many types of weeds such as *Enchinochloacrus galli* (L.), P. *Beauv, Urochloaplatyphylla, Digitaria* *spp. PanicumdichotomiflorumMichx., Cyperusiria L., Cyperusesculentus L., and some broadleaf weeds such as Physalis angulate L. and Polygonumlapathifolium D.* (Sudianto et al., 2013). Imidazolinone also reported to be efficient in controlling Orobanche weeds in legumes and sunflower (Goldwasser et al., 2003). In controlling the weeds, Imidazolinone herbicides will inhibit specific enzyme aceto hydroxy acid synthase and then cause the disruption of protein synthesis. These disruptions will interfere DNA synthesis and cell growth of the weeds plant (Chin et al., 2003).

The combined use of imidazolinone-resistant rice cultivars with the correspondent herbicides is often very effective, providing more than 95% of control of weedy rice in most cases. Mainly for weedy rice and the *Echinochloa complex*, this technology had permitted immediate benefits in terms of efficiency and easiness of weed control (Andres et. al, 2003).

2.3 EFFECTS OF USING IMIDAZOLINONE HERBICIDES

However, the application of herbicides for paddy field have becoming a serious issue nowadays. This is due to the negative effects imposed by the herbicides used by the farmers to the environment. Generally, based on the survey done in China, it is shown that herbicides caused physical harm to the farmers health(Qiao, Huang, Zhang & Rozelle, 2012). The harm can be in both visible and invisible effects. Examples of visible effects are vascular membrane on eye, lichenification and fissuring, wheezing cough, nausea and vomitting. Meanwhile, examples of invisible effects such as elevation of creatinine, elevation of urea nitrogen, and abnormality of cholinesterase.

Furthermore, herbicides can also harm the other living creatures such as animals, insects, and plants. According to Norton, Heong, Johnson, & Savary (2010), the environmental effects of herbicide application are as follow:

- the number of aquatic vertebrates declines rapidly with herbicide use;
- herbicide residues in surviving populations of vertebrates tend to be low;
- invertebrate populations suffer relatively small effects due to a reduction in predator populations such as fish and frogs;

- worm populations decline, which reduces fish food and soil aeration;
- algae blooms occur at first but later decline;
- long-term detrimental effects on microbial populations are few;
- Pest predator balance is disrupted, leading to pest resurgence and development of secondary pest problems.

Fortunately, imidazolinone herbicides used is are not harmful to human and animals (Santos, 2014). However, Imidazolinone herbicides can contaminate the environment. Imidazolinone are recognized by their herbicidal effect at low dose, covering a wide spectrum of weed control and high soil persistence. Imazapic and imazapyr mixture is considered as the most persistent herbicide in soil compared to the other herbicides. It is reported that soil persistence of Imazapyr may vary from 90 to 730 days and soil persistence of Imazapic is about 90 days after been applied (Alister & Kogan, 2003). This soil persistence is positive when it can control the weeds longer but it will become undesirable when its residual activity can result in injury to crops planted in succession or rotation (Santos et al., 2014). Commonly, in Malaysian condition, the rice will be cultivated 2 to 3 times in a year and the seeds will be replaced after a few years after the present of the herbicide tolerant weedy rice. These situation lead to the non-imidazolinone resistant new seeds or crops introduced afterwards, been potentially injured by the herbicides. There are injury reported had been occurred to rotational crops such as rice, alfalfa, cotton, oats, rye, potatoes, sugar beet, canola, onions, pea, sunflower, flax, melon, maize, mustard, pepper, cabbage, sorghum, wheat, tomatoes, vetch, white clover, birdsfoot trefoil and tall fescue due to residual activity of imidazolinone herbicide (imazethapyr + imazapic or imazapyr + imazapic). Mixture of Imazapyr and Imazapic is believed to produce more carryover than the mixture of imazethapyr and imazapic independent to the volume of dose used (Santos et al., 2014).

Furthermore, the imidazolinone herbicides have a high contamination potential of surface and ground waters. This is happened due to imidazolinone high persistence and water solubility that will increase their mobility in the environment (Martini , 2013).The surface water is contaminated through herbicides residue in the irrigation system while for the groundwater is through deep percolation of herbicides (Bouwer, 1987). In most of the rice farms, the herbicide applications is followed by the irrigation which depending on the handling of the water and on the occurrence of rain. There is a risk that part of the applied herbicide will be carried out of the area and contaminate water sources (Zanella, 2011). Application of imazapyr will pose a risk to all plants outside of the target area, where spray drift is possible. Care should be taken to minimise such drift and drift into natural watercourses close to the application area could also result in damage to non-target aquatic plants. Surface water pollution is affected by characteristics of rice fields, the climate conditions and the use of pesticides. Actions need to be taken to quantify their degree of occurrence and to implement measures to prevent it. The summary of groundwater contamination potential shown in **Table 2.3**.

Table 2.3: Summary of Groundwater Contamination Potential as Influenced by Water, Pesticide and Soil Characteristics

	Risk of Groundwater Contamination	
	Low risk	**High risk**
Pesticide characteristics		
Water solubility	low	high
Soil adsorption	high	low
Persistence	low	high
Soil characteristics		
Texture	fine clay	coarse sand
Organic matter	high	low
Macropores	few, small	many, large
Depth to groundwater	deep (100 ft or more)	shallow (20 ft or less)
Water volume		
Rain/irrigation	small volumes at infrequent intervals	large volumes at frequent intervals

2.4 ADSORPTION AND DESORPTION PROCESS

Major mechanisms affecting herbicides movement in soil are by adsorption and desorption(Sabatini & Austin, 1990). Soil sorption can affects the herbicides activity and soil persistence (Sun et al., 2012).Adsorption process can make the toxicants of herbicides less harmful and reduces leakage. Adsorption and desorption of herbicides is significant in influencing the fate of herbicide in soil environments through the interaction that occur between soil components and the herbicide Adsorption indicates how strongly an herbicide adheres to the soil components while moving down with water (Guzella, 2006). In general, adsorption is governed by a number of forces such as covalent bonding, electrostatic attraction, hydrogen bonding or non-polar interactions between the adsorbed species, lateral associative interaction, solvation and desolvation, therefore, the cumulative result of some or all of the above forces will give in the total adsorption value. This interaction will affect the herbicide movement, volatilization, degradation, bioavalability and transformation by biotic agents. Herbicide will react with the active sites that located on the soil surface. The very reactive site can hold the herbicide molecules strongly while the less reactive site will let the loosely herbicide molecules desorb (Wu et al., 2011). The adsorption and desorption process will occur simultaneously with the adsorption process has higher efficiency compare to desorption process.

Different soils have different adsorption properties.The adsorption and desorption of chemical compound are related to various properties of soil such as soil organic matter, type and amount of clay, ion exchange capacity, and soil pH including also some phsiochemical parameters such as water solubility, ocatanol-water partition coefficient, and pK_a (Wu et al., 2011). Soil with strong adsorption properties can be applied more herbicides(Stenersen, 2004).

According to Alister (2005), the sorption process of herbicide is affected by factors like soil moisture, soil pH, organic matter and soil type which is related to clay content in the soil. It is also supported by Oliveira et al., (2006) which stated that soil pH, clay and organic carbon content, particle size and the location of the soil in subsurface layer are affecting the soil sorption process. Besides that, Zheng et. al (2010) also found that solid/solution ratio and co-existence of other herbicide are affecting the adsorption process rate. In addition, the type of herbicides either they are weak base, weak acid or non-ionizable are affecting sorption process rate.For weak acid herbicides, they lose a proton and predominantly anions in soil, which has a pH range of 5 to 8 (Oliveira et. al, 2000).

Wu(2011) found that highest level of sorption of monosulfuron-ester are measured in soils with low pH, high organic carbon content and high clay contents while the lowest sorption is measured in soil with lower organic carbon content, lower clay content and high soil pH.

Stenersen (2004) stated that examples of good absorbent are humus, clay and active carbon. This type of absorbents have larger surface area which increase the contact surface area between the water on the surface with the soil.Soil adsorption is occurred due to colloidal fractions between clay minerals and organic matter. These materials have the potential to absorb molecules by ion exchange, coordination with metal exchange ions, hydrogen bonding, physical forces, and entropy effects(Grover, 2000). Amirianshoja (2013) found a relationship between the adsorption of the nonionic surfactant and the amount of clay minerals in the adsorbents. As the percentage of clay minerals in the adsorbents increased, the quantity of surfactant that was adsorbed by the adsorbents also increased. The adsorption power of clay minerals for the nonionic surfactant followed the rank order of montmorillonite > billite > kaolinite. Surface area is another factor that affecting the interaction between solid and liquid interfaces. The smaller clay particles do have larger surface area to provide more interaction between solid and liquid interfaces.

Increased sorption at low soil pH has been attributed to formation of herbicide cation for weak base herbicides. Soil pH is one of the the most important factor in determining the soil binding strength of the herbicides molecules. Soil adsorption is lower on neutral and high pH soils. At pH 6 to 9, an anionic form predominates which the herbicides molecules are weakly bound to the soil or repulsed due to negative charges presence in the soil colloids. As the soil pH decreases, supposely, the amount of neutral and cationic forms of the herbicides is increased and lead to higher soil adsorption process. At soil pH between 6 to 2.5, the herbicide is having a dominant form of double ion (Pintado, 2011).

Tiwari(2012) stated that the critical factor affecting the sorption of pesticide is soil organic matter. The soil with higher organic carbon has higher sorption capacity. More than 95% pesticides used which were endosulfan and chlorpyrifos are completely adsorbed within 12 hours duration. The initial pesticides concentration applied is also affecting the adsorption rate(Zhang, 2010). Experiments done previously shown that pesticide, which is imazethapyr, has faster pesticide's incubation time when the initial pesticide concentration is higher. Commonly, the pesticide is initially degrade rapidly and after that follow with slower phase.

Quantitatively, the adsorption can be measured using Freundlich's and Langmuir's adsorption isotherms which are :

Freundlich's adsorption equation

$$\frac{x}{m} = k \,.\, C^{n}$$

$$log\left(\frac{\mathrm{x}}{\mathrm{m}}\right) = \log(\mathrm{k}) + \mathrm{n}\,.\log(\mathrm{C})$$

x – Amount of chemical absorbed (in equlibrium)

m – weight units of soil

c – equilibrium concentration

k and *c* – constants

Langmuir's adsorption equation

$$\frac{Ce}{Cs} = = \frac{1}{Cm.KL} + \frac{\mathrm{Ce}}{Cm}$$

K_L- The Langmuir adsorption coefficient characterizing the adsorption-desorption capacity.

C_m – Maximum amount of herbicide adsorbed

C_s - Ratio of adsorption concentration in soil, (x/m)

x - The amount of Imazapyr adsorbed by a soil.

m – Weight of the soils, kg

C_e - The equilibrium concentration in solution

Imidazolinones herbicides are acidic herbicides and are not adsorbed extensively. They sorptiveness are governed by soil pH(Zimdahl, 2007). So, imidazolinones herbicides have higher adsorption rate in acidic soil pH. In acidic soils, imidazolinones molecules are in anionic form may developed a cationic connections with the positive oxides in the soil (Oliveira, Prates and Junior, 2006).Ulbrich (2005) also shows that both imazapic and imazapyr have high adsorption rate to the lower pH and greater clay content soil. These shows that, in Malaysia, the adsorption rate of imazapic and imazapyr can be increased by lowering the pH value and apply both herbicides in high clay content field.

On the other hand, in the equilibrium state, the herbicides will undergo desorption process. This process is the opposite of adsorption process. It is much slower process (Stenersen, 2004). This might happen since the pores present in the soil are very small thus make the herbicides not been easily extracted and decreasing bioavailability.

The desorption process occurs due to many factors. One of the factors is there are herbicides that do not bind much to the soil matrix and not absorb by the soil so that they will not be degraded by the microorganisms(Stenersen, 2004). The other factor is the soil texture itself , where desorption process is very common to occur in sandy soil with less content of clay and humus so that the soil become a weak herbicides absorbent. The quantitative value of desorption process can be calculated using the Freundlich's and Langmuir's adsorption isotherms.

The adsorption and desorption process can be enhanced by adding absorbent. Yedla(2008) proved that adsorbent such as wood charcoal can be used to increase the adsoption and desorption rate of pesticides such as endosulfan. Adsorbent helps to increase the carbon content in the soil.

2.5 RESEARCH GAP

Based on the cited literiture, it is important to study for the adsorption and desorption process of herbicides especially that been used in Malaysia which is Imazapic and Imazapyr and the factors affecting both process. There are less research done before which are focusing on the Malaysian paddy field condition. Most of the researches done previously are focusing on the adsorption and desorption of the other herbicides such as monosulfuron-ester (Wu, 2011), acetamiprid (Yu, 2011), fluridone (FLUN), and norflurazon (NORO). These herbicides have different properties compare to the imidazolinone herbicide. Furthermore, there are researchers such as which focusing on the imidazolinone herbicide such as imazaquin (Oliveira, 2006) and imazethapyr (Oliveira, 2001) which has different properties to Imazapyr and imazapic. These researches also had been done in other country such as Brazil which has different soil condition compare to Malaysian condition. Most of the researches done within the scope of imidazolinone herbicide are more focusing towards the comparative study between the effectiveness of imidazaolinone with the other type of herbicides. Moreover, there are also researches done almost similar to the Malaysian condition which focusing on the effectiveness of the Clearfield Production System (CPS) and the On Duty® herbicides but with different scope in investigating the impact and weaknesses of CPS and On Duty® herbicides in the country which applied it such as Italy, U. S., Brazil, Colombia, Costa Rica, Italy, Uruguay and Malaysia (Sudianto, 2013) and (Santos, 2014). Besides, there are a few studies that focusing directly to Imazapic and Imazapyr herbicides. There are studies done previously which are comparing the effectiveness between imidazolinone herbicides consist of the mixture of imazapic/imazapyr and imazethapyr/imazapic on the imidazolinone tolerance variety field. Its scope to compare the effect of different herbicide mixture and dose used to the growth of the variety (Santos, 2014). In addition, a few studies had been done on the adsorption and desorption of Imazapyr. Pusino (1997) had done the study on Italian soils, Gianelli (2014) on Argentinean soils and Tjitrosemito (1992) on Indonesian soils. However, Malaysian soils are having different properties from soil of the other country, which affecting the sorption process of the herbicides So, the study is aiming to investigate the adsorption and desorption of On Duty® herbicides which is imazapic and imazapyr within the Malaysian soil condition which they are applied in paddy fields.

CHAPTER 3

METHODOLOGY

3.1 SOIL COLLECTION AND PREPARATION

The soil samples had been taken fom the paddy field which is located in Seberang Perak,Perak. The paddy field was owned by Federal Land Consolidation and Rehabilitation Authority (FELCRA) Seberang Perak. The soil samples was taken from different plots in the fields since the paddy field is considered the largest field in Peninsular of Malaysia. The soil samples was labeled as 322, 327, 1 , 324, 321 and 328. There is also some sandy soil collected from the sweet potatoes farm near Universiti Teknologi PETRONAS (UTP) and labeled X-Mining soil. Different locations have different soil properties.The soil samples were left to be air-dried and grounded to pass through a 2-mm sieve before analysis.

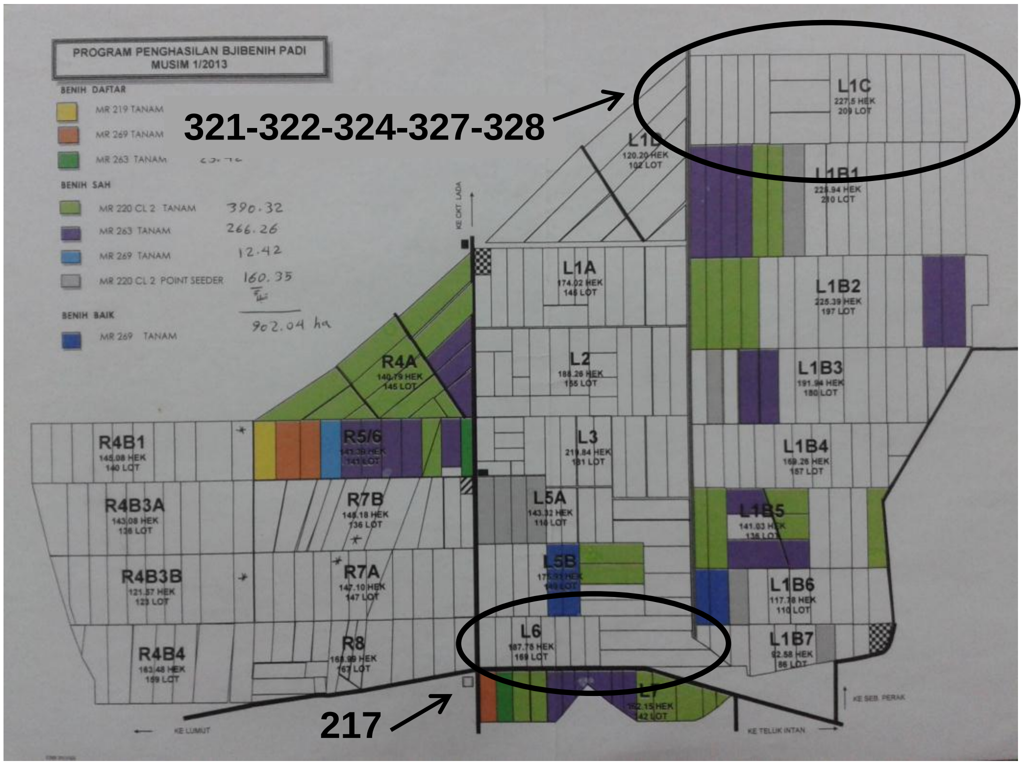


Figure 3.1: Location of the soil samples taken in Seberang Perak paddy fields.

Figure 3.2: Location of the X-mining soil samples taken in potatoes farm near UTP.

3.2 SOIL ANALYSIS

Investigation of the soils is done based on some related parameters that affecting the sorption process of the soil . The parameters are :

a) Soil Particle Size Distribution
b) pH of the soil
c) Organic carbon content of the soil
d) Exchangeable Ca+2, Mg+2 and K+ and CEC
e) Water Holding Capacity And Field Capacity (FC)

a) Soil Particle Size Distribution

The soil particle size distribution had be obtained through the conduction of pipet method. The purpose of this method was to determine the quantity of each of the main sand, silt, and clay fractions in samples of soil. For X-mining soil, the sieve analysis had been done to determine soil particle size distribution.

b) pH of the soil

The soil pH had been calculated using pH meter. The experimental procedures were as follow:

1) Soil pH was determined by taking 10 g of soil and mixing with 50 ml of distilled water.
2) The mixture was shaken for 15 minutes and left to stand overnight
3) The mixture's pH was measured using pH meter.

c) Organic carbon content of the soil

Organic carbon in the soils was determined by using non-dispersive, infrared, digital-controlled instrument Total Carbon Analyzer.

d) Exchangeable Ca^{+2}, Mg^{+2}, Na^{+} and K^{+} and Cation Exchange Capacity (CEC)

The exchangeable ca+2, mg+2 and k+ and CEC in the soil can be calculated using leaching method with ammonium acetate (NH_4OA_C) followed by potassium sulphate to measure soil CEC.

e) Maximum Water Holding Capacity (MWHC) and Field Capacity (FC)

The soil water holding capacity and field capacity (FC) can be calculated using pressure chamber and plate. The experimental procedures are as follow:

1) 10 grams of soils had been placed in a retaining ring.
2) The sample had been saturated for 24 h by keeping the water level just below the edge of the ring in a tray.
3) The plates with media sample were then placed inside the corresponding pressure chamber connected to an outflow tube.
4) Different levels of pressure were applied on each sample. For maximum water holding capacity, the pressure level was 0 kPa while the pressure for field capacity was 33 kPa.
5) The samples had been taken out when there were no dripping detected.

6) The samples weighted and oven-dried for 24 h and their dry weights recorded.

3.3 SORPTION STUDIES

3.3.1 Solution Preparation

A) Stock Solution

Stock solution of herbicide was prepared with concentration of 500 mg/l by adding 50 mg of the Imazapyr powder to 100 ml ultra pure water containing 110.99 mg Calcium Chloride ($CaCl_2$) and 20 mg Mercury Chloride ($HaCl_2$) to inhibit the soil microbial activity (Yu et.al., 2011).

B) Working Solution

Working solution is prepared by dilution of the stock solution. Working solutions will be prepared by dilution of the stock solutions with background water to make different concentrations of herbicide (0, 1, 2, 4, and 8 mg/l).

3.3.2 Batch Equilibration

Batch equlibration experiment was conducted to determine the capacity of each soil in sorption of herbicides. Besides, it could determine the equilibration time needed for sorption process to occur (Oliveira, 2006).

Duplicate 20-mL aliquots of 4 mg/l of Imazapyr working solution were added to 10 g of soil in 250-mL conical flasks and shaken at room temperature using rotary shaker at 150 to 200 rpm. Exceptionally, only 10-ml aliquots of Imazapyr working solution were added to 10 g of sandy soil.

1) The supernatant was removed from each tube after 1, 3, 6, 12 , 24 and 36 hours of soil-solution contact. The supernatant was centrifuged for 10 minutes at 7000 rpm and stored in freezer (-20^{o}C) until analysis.
2) Equilibration time was obtained when herbicide concentration remains constant.

3) Herbicide concentration was analyzed using HPLC.

There are two blank controls will be used during the experiments in order to monitor any loss during experiment. The result of this experiment can be used to design the batch equilibration experiment.

3.3.3 Single-Step Decant-Refill

Desorption experiments will be conducted by conventional single-step decant-refill technique (Yu, 2011).

1) After sorption reached equilibrium, the tubes were centrifuged and 10 mL of the supernatant in each tube will be taken out for analysis. The supernatants are stored in freezer (-20^{o}C) until analysis.

2) Another 10 mL of a solution, mixture of 200 mg Mercury Chloride and 1109.9 mg Calcium Chloride, was added into each tube.

3) After shaken for another 24 h and then centrifuged at 7000 rpm for 10 min, the herbicide desorbed from soils and stored in freezer (-20^{o}C) until HPLC analysis.

The experiments are done in duplicate. There are two blank controls will be used during the experiments in order to monitor any loss during experiment.

3.3.4 High Performance Liquid Chromatography (HPLC)

HPLC experiment is done to analyze the Imazapyr concentration in the supernatant, taken from Batch equilibration and Single-Step Decant-Refill.

1) Supernatant is analyzed directly by injecting 20µL of Imazapyr solution into a 15 cm by 4.6 mm ODS Adsorbosil C18 column.
2) Isocratic elutions were performed at a 1 mL min-1 flow rate, with a mobile phase consisted of 35% acetonitrile and 65% 1.0% acetic acid. It was detected at 240 nm wavelength.

3) The amount of Imazapyr sorbed to soil was calculated from the difference between the initial and remaining concentration in solution after equilibration.
4) The concentration of Imazapyr in the supernatant was obtained by interpolating the area under the Imazapyr peak in the graph within the calibration graph of standard Imazapyr solution.

Initially, HPLC analysis was run on the standard Imazapyr solution with concentration of 0, 0.5, 1, 1.5, 2, 4, 5, 6, 7 and 8 mg/l to obtain the calibration curve.

3.4 GANTT CHART

Semester 1 (14 weeks)

NO	DETAIL/WEEK	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	**Selection of Project Topic**	🟨	🟨												
2	**Preliminary Research Work**		🟨	🟨	🟨	🟨	🟨	🟨	🟨						
3	**Submission of Extended Proposal**						🟩								
4	**Proposal Defence**										🟩				
5	**Project Work**														
	5.1 Purchase of Material							🟨	🟨	🟨					
	5.2 Soil Investigation									🟨	🟨	🟨	🟨	🟨	🟨
6	**Submission of Interim Draft Report**													🟩	
7	**Submission of Interim Report**														🟩

Semester 2 (14 weeks)

NO	DETAIL/WEEK	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	**SOIL PREPARATION**	🟨													
2	**SOIL INVESTIGATION**														
	Soil Particle Distribution	🟨	🟨	🟨											
	Water Holding Capacity and Field Capacity(FC)	🟨	🟨	🟨											
	pH of the soil	🟨													
	Organic Content of the Soil		🟨												
	Soil Electrical Conductivity	🟨													
	Exchangeable ca^{+2}, mg^{+2} and k^{+} and Cation Exchange Capacity (CEC)				🟨	🟨	🟨	🟨	🟨						
	Exchangeable Al^{3+}, H^{+} and Effective Cation Exchange Capacity(ECEC)				🟨	🟨	🟨	🟨	🟨						
	ElementalCompositions				🟨	🟨	🟨	🟨	🟨						
	Micronutrients in Soil				🟨	🟨	🟨	🟨	🟨						
3	**ADSORPTION AND DESORPTION EXPERIMENT**														
	Batch Equilibration + High Performance Liquid Chromatography (HPLC)					🟨	🟨				🟨	🟨			
	Single-Step Decant-Refill + HPLC					🟨	🟨				🟨	🟨			

4	**PROGRESS REPORT**							🟨							
5	**PRE-SEDEX PRESENTATION**										🟨				
6	**SEDEX**												🟨		
7	**TECHNICAL PAPER**													🟨	🟨
8	**VIVA PRESENTATION**													🟨	🟨
9	**DISSERTATION REPORT**													🟨	🟨

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Soil Physical Properties

Soil Particle Size Distribution

Particle size distribution refers to the proportions by dry mass of a soil distributed over specified particle-size ranges. Soil particles usually been distributed into two type of particles which are coarse textured soils and fine textured soils. Coarse textured soils are represented by sand and gravels while fine textured soils are represented by clay and silt. Determination of soil particle size distribution is important to determine the soil function in engineering and agricultural purposes since particle size influences how fast or slow water or other fluid moves through a soil. In sorption reaction, different soil particle size will give different sorption rate. Fine particle soil will give more surface area available for sorption to occur compare to coarse particle.

Soil 1, 321, 322, 324, 327 and 328

Table 4.1 was the result of soil particle distribution for Soil 1, 321, 322, 324, 327 and 328. The percentage of clay, silt and sand particles were determined for each soil sample to be used to classify them by interpolation in USDA soil texture triangle table. The particles size was different for each gradation. Clay particles size was less than 2mm, followed by silt particles was in between 2 to 50 mm and the largest soil particle which is sand with size larger than 50mm.

Based on the soil particle size distribution results, there were 3 types of soil classification that been detected. There was clay soil which represented by 322, 324, 321 and 1 soil samples. There were also sandy clay loam and clay loam soils which were represented by 328 and 327 respectively.

Furthermore, there were 3 soil samples which had clay content greater than 50%. Soil sample 1 had the highest clay content with 71.27%, followed by 322 and 321 with 58.50% and 59.96% respectively. There was also one soil sample which had sand percentage greater than 50%. The soil sample was 328 with 55.30% sand percentage. There were absent of soil which silt percentage greater than 50%.

Table 4.1: The soil particle size distribution for soil samples.

Sample	Clay (%)	Silt (%)	Sand (%)	Soil Texture Class (based on USDA)
	Particle Size<2 mm	Particle Size 2-50 mm	Particle Size>50mm	
322	58.5	20.55	20.91	clay
324	45.65	18.58	34.49	clay
321	59.96	23.93	16.06	clay
1	71.27	26.29	2.35	clay
328	26.3	18.29	55.3	sandy clay loam
327	37.99	21.58	40.29	clay loam

Based on the soil classification, for further analysis, soil sample 328 and 327 had been selected due to their different of soil index. They were needed to investigate the sorption rate for sandy clay loam and clay loam typed soils. For clay soils, the selection had been done among soil 322, 321, 1 and 324 based on their soil pH.

X-mining Soil

Table 4.2 and **Figure 4.2** show the particle size distribution of X-mining soil.

Table 4.2: The soil particle size distribution for X-mining soil samples.

SIEVE SIZE	WEIGHT OF SIEVE (g)	WEIGHT OF SIEVE + SAND (g)	WEIGHT OF SAND RETAINED (g)	% SAND WEIGHT RETAINED	% SAND WEIGHT PASSING
3.35 mm	483.7	580	96.3	6.43	93.57
2.00 mm	473.1	614.9	141.8	9.46	84.11
1.18 mm	436	640.8	204.8	13.67	70.45
600 µm	405.7	660.3	254.6	16.99	53.46
425 µm	370.4	520.4	150	10.01	43.45
300 µm	358.2	550.6	192.4	12.84	30.61
212 µm	345.9	515.9	170	11.34	19.27
150 µm	333.5	458.4	124.9	8.33	10.94
63 µm	410.1	543.1	133	8.87	2.06
Pan	392	422.9	30.9	2.06	0.00
TOTAL SAND WEIGHT			1498.70 g		

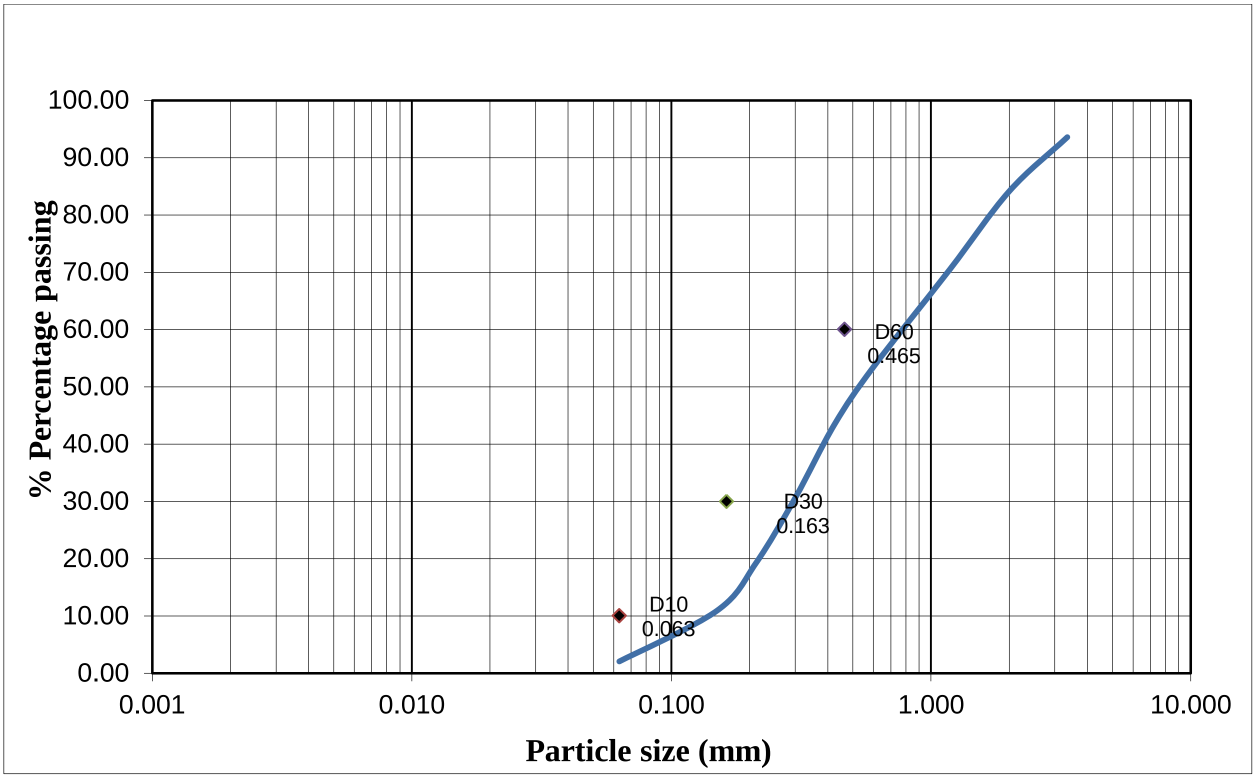


Figure 4.1: The soil particle size distribution graph for X-mining soil samples.

Based on the sieve analysis graph, it can be observed that the X-mining soil had an even curve on the gradation graph which could be classified as a dense gradation. This was due to X-mining soil had approximately equal amounts of various sizes of aggregate. A dense gradation soil had most of its air voids filled with particles. The X-mining soil consisted of gravel and sand particles only. There were sand particles with 82.05% and gravel particles with 9.46%.

Soil pH

Soil pH is a measure of the acidity and alkalinity in soils. Soil pH has a range from 0 to 14 with 7 as the neutral point. Soil pH less than 7 is considered acidic while soil pH greater than 7 is considered alkaline or basic. pH is very important variable in soil. Soil pH controls many chemical processes that take place in soil.

Furthermore, soil pH is one the main factor that affects the sorption process. There are some herbicide which favors acidic soil for sorption while there are some which favors alkaline or basic soil. Table shows the pH of all the soil samples.

Table 4.3: The soil pH.

SAMPLE	pH
322	6.76
328	5.433
327	5.85
X-mining	6.987
1	5.627
321	5.997
324	6.3

Based on the soil pH results obtained, The 328 soil has the lowest soil pH with 5.433. The X-mining soil has the highest soil pH with 6.987. Soil 328 and 327 is in acidic form while soil 322 and X-mining is either in neutral or alkaline form. Since selected soil samples 328 and 327 had pH lower than 6, thus, soil sample 322 was selected to represent clay typed soil for further analysis to determine the sorption study for high soil pH sample.

Organic Carbon Content of the Soil

Soil carbon is the generic name for carbon held within the soil, primarily in association with its organic content. Soil organic carbon enters the soil through the decomposition of plant and animal residues, root exudates, living and dead microorganisms, and soil biota. Thus, soil organic carbon is capable of decay and is the product of decay.

Furthermore, soil organic carbon can improves the physical properties of soil. It increases the cation-exchange capacity (CEC) and water-holding capacity of sandy soil, and contributes to the structural stability of clay soils by helping to bind particles into aggregates.

The soil total organic carbon was obtained by subtracting the percentage value of inorganic carbon from the percentage value of total carbon in the soil. It was difficult to obtain the percentage value of total organic directly. Table showed the result of the percentage value of soil total organic carbon.

Table 4.4: The soil organic carbon content (%).

SAMPLE	TOTAL CARBON (%)	INORGANIC CARBON (%)	TOTAL ORGANIC CARBON (%)
322	0	0	0
328	0.1021	0.02306	0.07904
327	0	0	0
X-mining	0.3082%	0.0209%	0.2873%

The X-mining soil had the highest total organic carbon (TOC) with 0.2873%. Soil 322 and 328 had 0 % percentage probably to its lower organic carbon content, the instrument could not detect the value. It was almost impossible if there were absent of organic carbon inside agricultural soil. Soil sample 328 had about 0.07904% of total organic carbon content.

Water Holding Capacity and Field Capacity (FC)

Soil water holding capacity is the amount of water that a given soil can hold for crop use while field capacity is the point where the soil water holding capacity has reached its maximum for the entire field. Soil texture, clay type and organic matter are the key components that determine soil water holding capacity. The soil's water holding capacity is strongly related to particle size. Soil made up of smaller particle sizes, such as in the case of silt and clay, have larger surface area thus make it easier to hold onto water so that it has a higher water holding capacity. Sand in contrast has large particle sizes which results in smaller surface area and low water holding capacity. **Table 4.5** shows the water holding capacity and field capacity for 322, 327, and 328 soil samples.

The pressure value applied to the chamber for maximum water holding capacity determination was at 0 kPa. Meanwhile, for field capacity determination, the pressure applied was at 33 kPa. The 322 soil has the highest water holding capacity value with 46.67157 % while 328 soil has the lowest value with 39.432 %. The 322 soil has the highest water holding capacity value with 29.96336% while 328 soil has the lowest value with 21.61013%. Logically, 322 soil had more clay content compare to 327 and 328 soil. So, it could retain more water compare to the other soil samples.

Table 4.5: The water retention percentage for soil samples 322, 324, 321, 1, 327 and 328.

SAMPLE	MAXIMUM WATER HOLDING CAPACITY (%)	FIELD CAPACITY (%)
322	46.67	29.96
328	39.43	21.61
327	43.16	26.68

Exchangeable Ca^{+2}, Mg^{+2}, Na^{+} and K^{+} and Cation Exchange Capacity (CEC)

Cation exchange capacity (CEC) is the capacity of soils to hold positively charged ions such as calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^{+}), and sodium (Na^{+}). These cations are held by the clay and organic matter particles in the soil through electrostatic forces. Clay particles generally have a negative charge, so they attract and hold positively charged nutrients and non-nutrients. Soil organic matter has both positive and negative charges, so it can hold on to both cations and anions. The cations on the CEC of the soil particles are easily exchangeable with other cations. Thus, the CEC of a soil represents the total amount of exchangeable cations that the soil can adsorb. The cations used by plants in the largest amounts are calcium, magnesium, sodium, and potassium. Generally, a sandy soil with little organic matter will have a very low CEC while a clay soil with a lot of organic matter will have a high CEC. **Table 4.6** shows the exchangeable cation **(**Ca^{+2}, Mg^{+2}, Na^{+} and $K^{+)}$ and Cation Exchange Capacity (CEC) of the soils.

Based on the exchangeable cation and CEC results obtained, soil 322 had the highest CEC with 16.44 cmol(+)/kg, followed by soil 328 with 14.01 cmol(+)/kg, then, soil 327 with 12.55 cmol(+)/kg and last was X-mining soil with very low CEC value which was 1.84 cmol(+)/kg. Logically, soil 322 had the highest amount of clay compare to the other soils which was 58.5%, thus soil 322 could hold more cations compare to the other soil. In addition, with the absent of clay particles and low total organic carbon content, so, X-mining soil did have low CEC value.

Table 4.6: The exchangeable cation **(**Ca^{+2}, Mg^{+2}, Na^{+} and K$^{+)}$ and Cation Exchange Capacity (CEC) of the soils.

TYPE	EXCHANGEABLE CATION(cmol(+)/kg)				CATION EXCHANGE CAPACITY,CEC (cmol(+)/kg)
	K^+	Ca^{2+}	Mg^{2+}	Na^+	
322	0.62	6.5	3	0.09	16.44
328	0.41	6.17	2.26	0.07	14.01
327	0.37	5.73	3.33	0.06	12.55
X-mining SOIL	0.18	1	0.35	0.05	1.84

As summary, all the physiochemical properties of all the soil samples are listed and shown in **Table 4.7**.

Table 4.7: Summary of soil properties.

TYPE	pH	TOC (%)	CLAY CONTENT (%)	SILT CONTENT (%)	EXCHANGEABLE CATION(cmol (+)/kg)				CEC (cmol (+)/kg)
					K^+	Ca^{2+}	Mg^{2+}	Na^+	
322	6.76	0	58.5	20.55	0.6	6.5	3	0.09	16.44
328	5.43	0.07904	26.3	18.29	0.4	6.2	2.3	0.07	14.01
327	5.85	0	37.99	21.58	0.4	5.7	3.3	0.06	12.55
X-MINING SOIL	6.99	0.002873	0	0	0.2	1	0.4	0.05	1.84

4.2 High Precision Liquid Chromatography (HPLC) Standard

HPLC is a separation technique that involves the injection of a small volume of liquid sample into a column tube packed with tiny particles, where individual components of the sample are moved down the packed tube with a liquid, the mobile phase, forced through the column by high pressure delivered by a pump. These components are separated from one another by the column packing that involves various chemical and/or physical interactions between their molecules and the packing particles. These separated components are detected at the exit of this column tube by a flow-through device that measures their amount. The output from the detector is called a "liquid chromatogram".

Initially, the first HPLC analysis needs to be done on the standard Imazapyr solution, the one which are not undergoing sorption process. This analysis is important to know the behavior of the Imazapyr since each compound had different behavior. The behavior can be determined from the chromatogram that will be obtained after the analysis. Since there are salt present in the solution from the reaction of Calcium Chloride and Mercury Chloride, so, it is required to check which one is the peak of the salt and the peak of Imazapyr.

Figure 4.2 shows the chromatogram of standard Imazapyr solution.

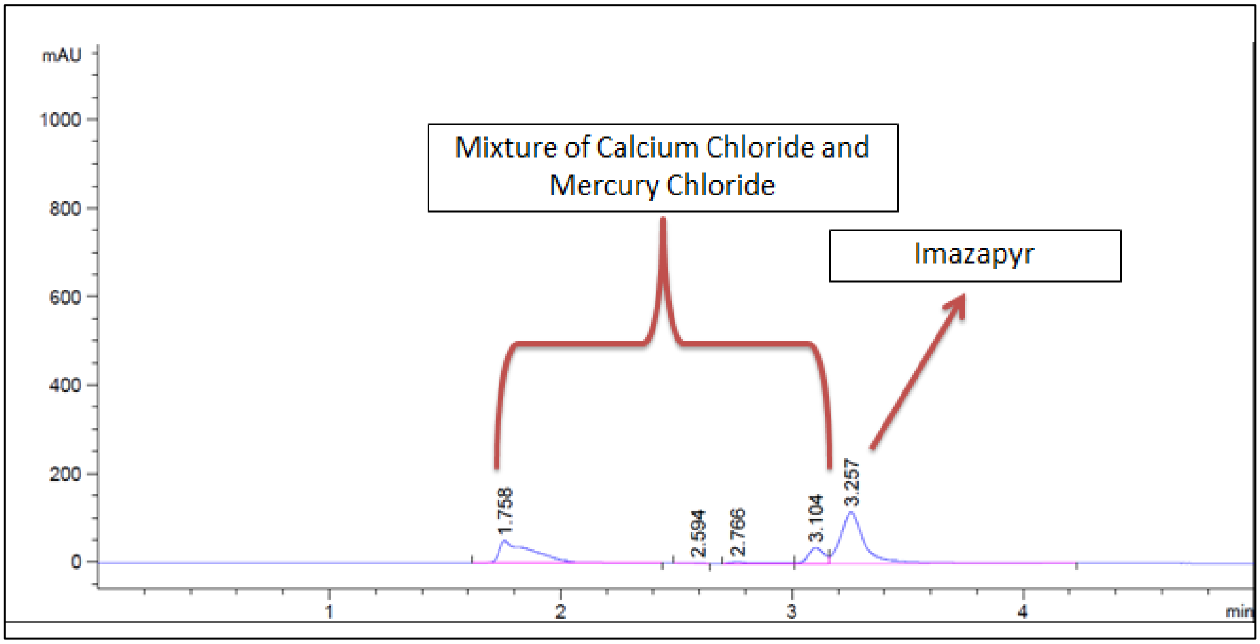


Figure 4.2: The Imazapyr chromatogram.

Based on the chromatogram of the stock solution of Imazapyr, it was observed that the retention time for Imazapyr was around 3 to 3.5 minutes. Due to injection limit which was at 20 µL, the Imazapyr peak that obtained was small. For obtaining the concentration of Imazapyr, only the area under graph for Imazapyr peak was integrated

This analysis was required for latter stage in plotting the calibration graph for determining the concentration of the sorption samples. A few standard Imazapyr solution which were 0, 0.5, 1, 1.5, 2, 4, 5, 6, 7 and 8 mg/l had been prepared. The wider the range of Imazapyr concentration analyzed, the more accurate the calibration graph could be plotted.

Figure 4.3 shows the calibration curve for Imazapyr solution with vary concentrations.

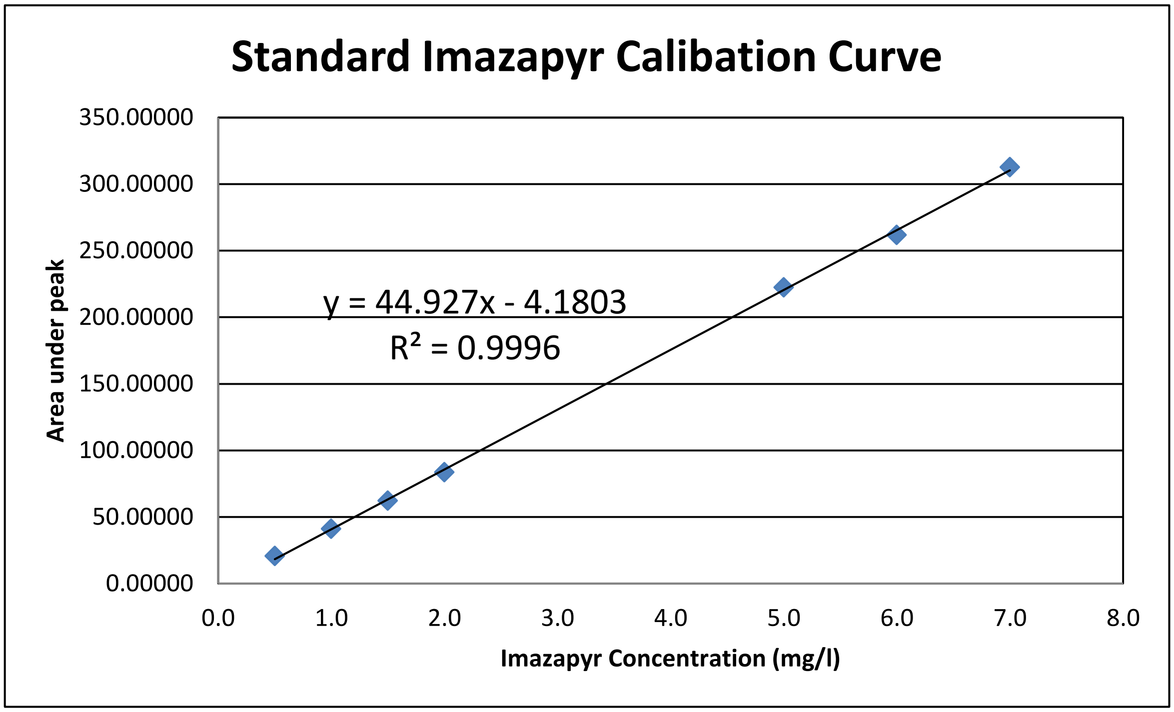


Figure 4.3: The Imazapyr concentration calibration curve.

This was the calibration curve that had been plotted on the standard Imazapyr solution with different concentration. The graph was plotted on Imazapyr concentration of 0, 0.5, 1, 1.5, 2, 4, 5, 6, 7 and 8 mg/l. The line graph equation of the calibration curve was as below:

$$y = 44.927x - 4.1803$$

The correlation value was significant with R^2 value of 0.9996. This graph was required to determine the Imazapyr concentration for sorption studies by interpolation using the line equation.

4.3 Equilibrium Time Determination

Equilibrium time for the sorption study is determined when the concentration of Imazapyr in the solution remained constant. At equilibrium time, the soil sorption capacity is already at its maximum rate. There are no adsorption occur between the solution and the soil. All the soil particles are already binded with the Imazapyr molecules.

Equilibrium time is important to be known since it is needed for latter stage in designing the batch equilibration and single-step decant-refill experiments. It is very important to design the experiments with the maximum duration and capacity for soil sorption to occur.

Figure 4.4 shows the batch equilibration experiment result to determine the equilibrium time for adsorption study.

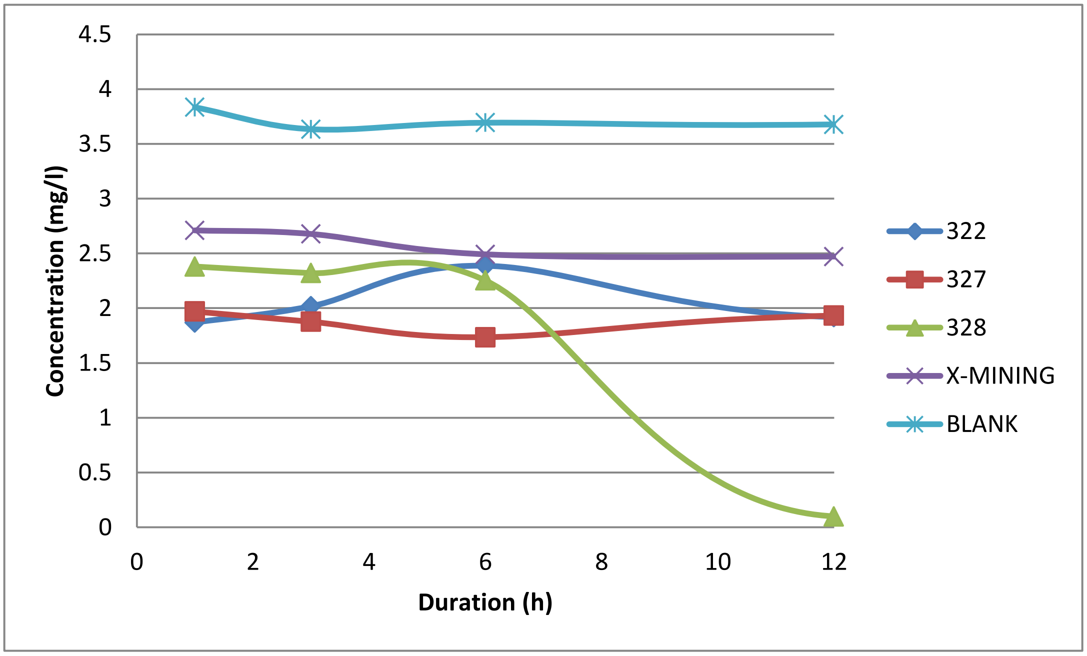


Figure 4.4: The Imazapyr residue concentration after adsorption process.

The initial batch equilibration experiment was done to determine the equilibration time for sorption process to occur. Equilibration time was obtained when herbicide concentration remained constant. It showed that no more adsorption was occurring after the equilibrium time.

Based on the results obtained, the equilibration time obtained was not quite clear and significant. This was happen due to some missing data for 24 and 36 hours duration samples during the HPLC analysis. Generally, the equilibration time could be observed for blank and X-mining soil sample which was around at 6 hours duration. For 322, 328 and 327, the equilibration time could be determined. The Imazapyr concentration of these soil samples did not remain constant within the 12 hours duration. For most of the soil samples, the adsorption rate was much higher at the early stage of the experiment which was around 0 to 5 hours. There were also some soil samples which were undergoing desorption process within the 12 hours duration. According to Wu (2011), the adsorption and desorption happened at the same time. When mixed with soils, herbicides molecules will react with available active sites on soil particles surfaces. There are some which were very reactive, so that they can hold pesticide molecules strongly, while others are not reactive enough, thus, pesticide molecules became loosely bounded and desorbed. However, the adsorption efficiency was greater than the desorption efficiency

Since the equilibrium time obtained was not significant, based on data obtained from previous researches such as Wu (2011), Oliveira (2006), and Tiwari (2012), for laboratory convenience, 24 hours was taken as the equilibration time.

Figure 4.5 shows the single-step decant-refill experiment results to determine equilibrium time for desorption study.

The first single–step decant-refill experiment was done to determine the equilibrium time for desorption process. There were no significant time to indicate the equilibration time for the desorption process. The Imazapyr concentration inside the supernatant was still keep increasing. There were no signs that the concentration will keep constant even after the experiment time limit which was at 36 hours duration. Based on the adsorption process, for laboratory convenience, 24 hours was taken as the equilibration time for desorption study.

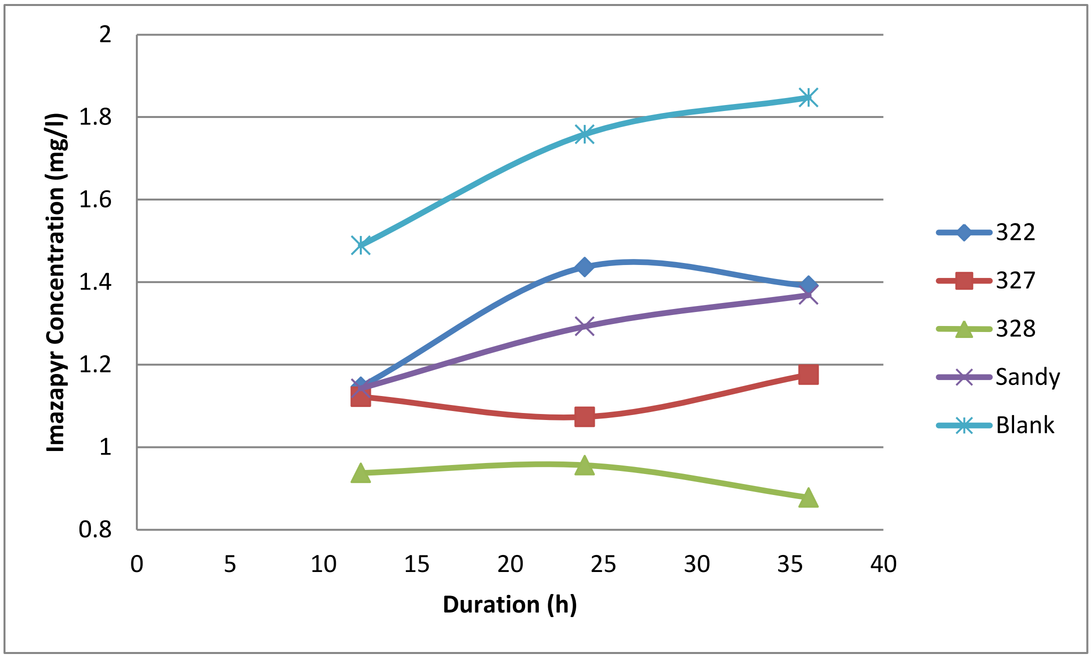


Figure 4.5: The Imazapyr residue concentration after desorption process.

4.4 Sorption Model Isotherm

Freundlich Isotherm Model

The Freundlich isotherm model was plotted based on the following linearised Freundlich isotherm equation

$$\log Cs = \frac{1}{n}\log Ce + \log Kf$$

K_f - The adsorption coefficient characterizing the adsorption-desorption capacity.

n - The Freundlich equation exponent related to adsorption intensity that is used as an indicator of the adsorption isotherm nonlinearity.

C_s - The amount of Imazapyr adsorbed by a soil.

C_e - The initial equilibrium aqueous concentrations.

The Freundlich adsorption isotherms are shown in **Figure 4.6**, and their parameters K_f, l/n and R^2 are shown in **Table 4.8**.

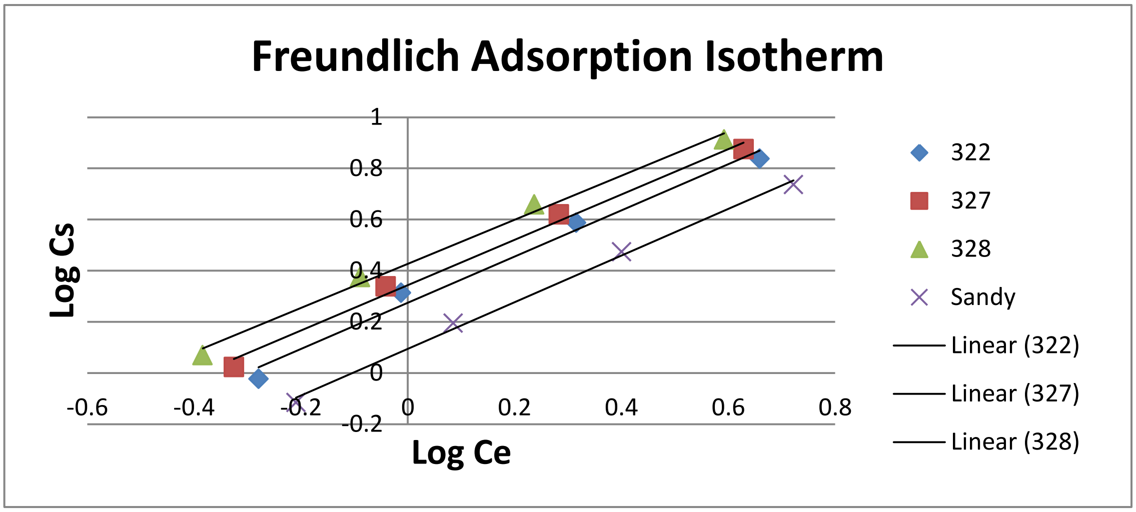


Figure 4.6: Freundlich Adsorption Isotherm for all the soil samples.

Langmuir Isotherm Model

The Langmuir isotherm model was plotted based on the following linearised Langmuir isotherm equation

$$\frac{Ce}{Cs} = = \frac{1}{Cm.KL} + \frac{\mathrm{Ce}}{Cm}$$

K_L- The Langmuir adsorption coefficient characterizing the adsorption-desorption capacity.

C_m – Maximum amount of herbicide adsorbed

C_s - Ratio of adsorption concentration in soil, (x/m)

x - The amount of Imazapyr adsorbed by a soil.

m – Weight of the soils, kg

C_e - The equilibrium concentration in solution

The Langmuir adsorption isotherms are shown in **Figure 4.7**.

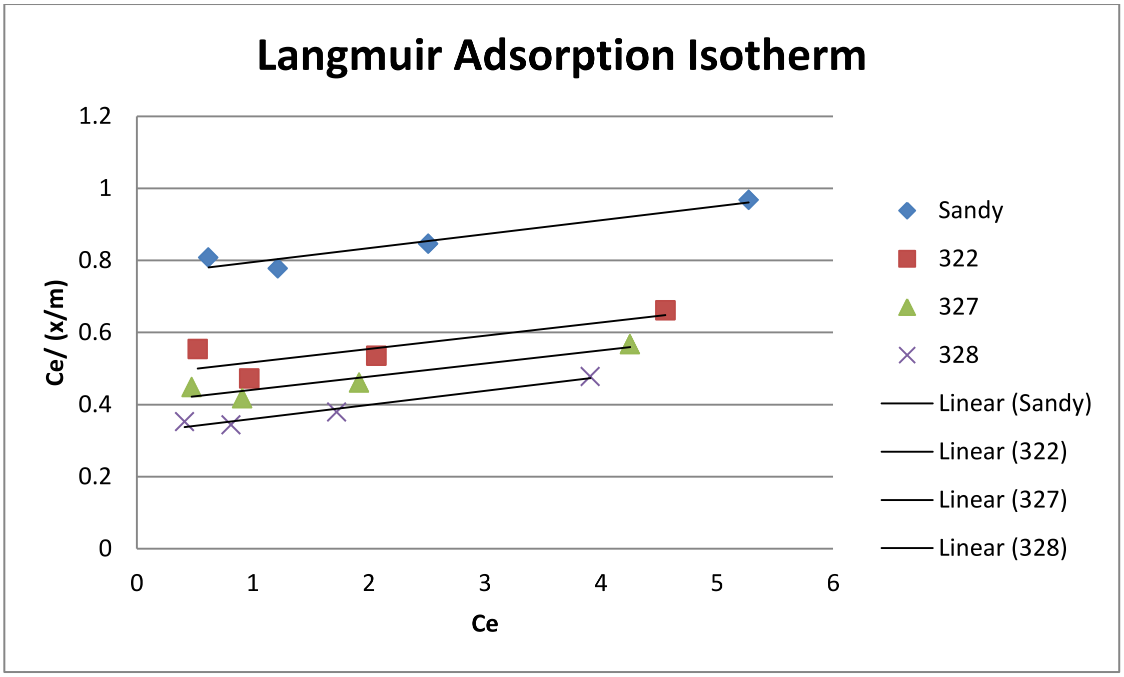


Figure 4.7: Langmuir Adsorption Isotherm for all the soil samples.

Table 4.1 shows the equation and correlation coefficient of Freundlich and Langmuir adsorption isotherm.

Table 4.8: Equation and Correlation Coefficient of Freundlich and Langmuir Adsorption Isotherm

Soil	Freundlich Adsorption		Langmuir Adsorption	
	Equation	R^2	Equation	R^2
322	y = 0.9027x + 0.2751	0.9846	y = 0.0366x + 0.4811	0.7037
327	y = 0.887x + 0.3432	0.9918	y = 0.0364x + 0.4045	0.8915
328	y = 0.8616x + 0.4274	0.9932	y = 0.0388x + 0.3214	0.9631
X-mining soil	y = 0.9117x + 0.0944	0.9967	y = 0.0387x + 0.7565	0.9275

Based on the **Table 4.8**, the coefficient correlation, R^2 of Freundlich isotherm was within range of 0.986 to 0.996 while for Langmuir isotherm was within 0.704 to 0.963. It was shown that the adsorption data was better fit the Freundlich adsorption isotherm. So, the further analysis on the sorption study was done based on the Freundlich adsorption isotherm. **Table 4.9** shows the parameters K_f, l/*n* and R^2 of Freundlich adsorption isotherm.

Table 4.9: parameters K_f, l/*n* and R^2 of Freundlich Adsorption Isotherm.

Sample	log K_f	$K_{f\ ads}$	$1/n_{ads}$	R^2
322	0.2751	1.884082866	0.9027	0.9846
327	0.3432	2.203941182	0.887	0.9918
328	0.4274	2.675469473	0.8616	0.9932
X-mining	0.0944	1.242796438	0.9117	0.9967

Based on the Freundlich linear isotherm graph obtained, all the graph correlations were significant with R^2 value > 0.98. It indicated that the adsorption equilibrium of imazapyr on the 4 soil samples for 24 hour fit the empirical Freundlich equation. The soil sample adsorption rate was determined based on the value of K_f. Overall, the K_f value for all the soil samples was in the range of 1.2 to 2.7. The arrangement started with the higher adsorption rate was 328 > 327 > 322 > X-mining soils. The soil with the highest adsorption was 328 K_f with value of 2.676. Soil 328 was the soil with the lowest pH value and higher organic carbon content compare to the other soil samples. The soil with the lowest adsorption rate was X-mining with K_f value of 1.243. It was expected that the X-mining soil, which represent the sandy soil group, would have low adsorption rate. In addition, X-mining was the soil with higher soil pH and absent of silt and clay particles.

The 1/n parameter is a measure of the nonlinearity of the sorption isotherm (Gianelli, 2014) .The values of 1/n ranged from 0.887 to 0.912, which show that all the isotherms were non-linear. The condition of non-linear was the 1/n < 1. Since 1/n is less than 1, the Freundlich equation describes adequately the sorption isotherm (Gianelli, 2014). Based on 1/n value obtained, it is either convex or L-type isotherm were observed (Pusion, 1997). According to Wu (2011), convex isotherm contends with a modification of the affinity between pesticide molecules and soils when increasing concentration while an L-type isotherm suggests a relatively high affinity of the herbicide for the adsorbing sites. When solution concentration increased, accessibility to free sorption sites decreased and led to a decreasing of the absorbed amounts by soils.

Freundlich Desorption Model Isotherm

The Freundlich desorption model isotherm was plotted and calculated using the same equation and relation in the adsorption study. The K_f will be analyzed inversely since the equation used was based on the amount of Imazapyr adsorbed to the soil. In desorption process, the soil with the highest desorption rate is the soil with the less amount of Imazapyr absorbed to the soil. Thus, the soil with the lowest K_f value was the soil with the highest desorption rate. Otherwise, the soil with highest K_f value was the soil with lowest desorption rate.

Figure 4.8 shows the Freundlich desorption isotherm.

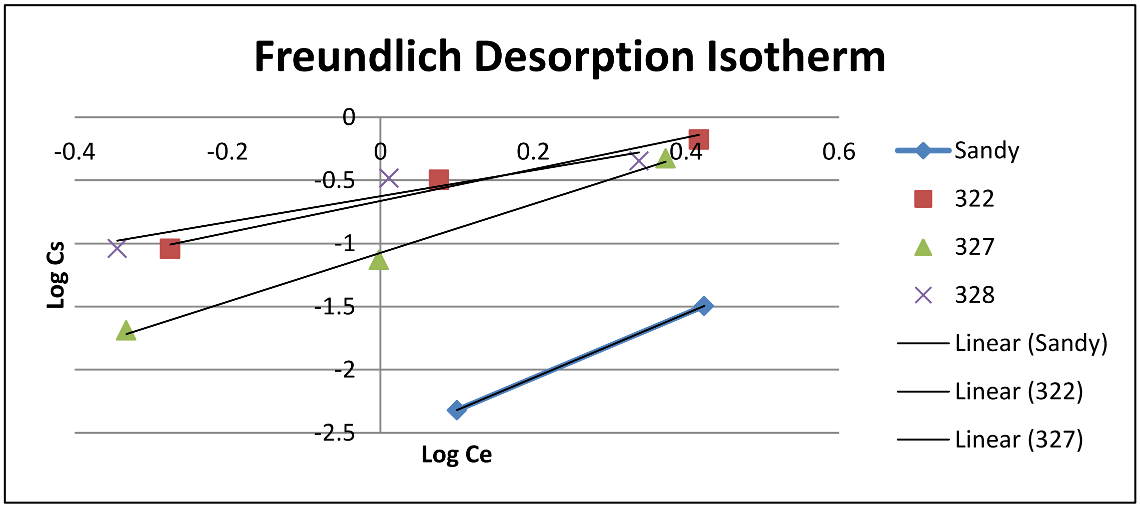


Figure 4.8: Freundlich desorption isotherm for all the soil samples.

Langmuir Desorption Model Isotherm

The Langmuir desorption model isotherm was plotted and calculated using the same equation and relation in the adsorption study. The K_L will be analyzed inversely since the equation used was based on the amount of Imazapyr adsorbed to the soil. In desorption process, the soil with the highest desorption rate is the soil with the less amount of Imazapyr absorbed to the soil. Thus, the soil with the lowest K_L value was the soil with the highest desorption rate. Otherwise, the soil with highest K_L value was the soil with lowest desorption rate.

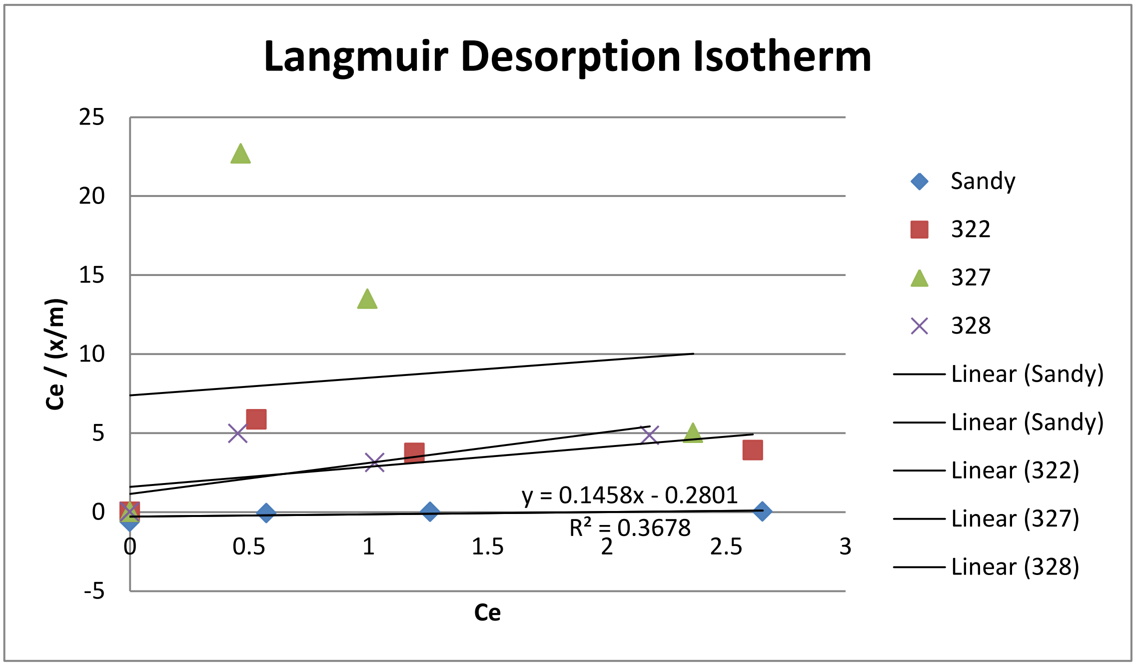


Figure 4.10: Langmuir desorption isotherm for all the soil samples.

Table 4.10 shows the equation and correlation coefficient of Freundlich and Langmuir adsorption isotherm.

Table 4.10: Equation and Correlation Coefficient of Freundlich and Langmuir desorption isotherm

Soil	Freundlich Desorption		Langmuir Desorption	
	Equation	R^2	Equation	R^2
322	y = 1.2549x - 0.6629	0.9804	y = 1.2751x + 1.5967	0.2858
327	y = 1.9355x - 1.074	0.9953	y = 1.1176x + 7.3858	0.0126
328	y = 1.0248x - 0.6254	0.9059	y = 1.9632x + 1.1504	0.5258
X-mining soil	y = 2.5507x - 2.5767	1	y = 0.1458x - 0.2801	0.3678

Based on the Table 4.10, the coefficient correlation, R^2 of Freundlich isotherm was within range of 0.980 to 1 while for Langmuir isotherm was within 0.013 to 0.526. It was shown that the desorption data was better fit the Freundlich desorption isotherm. So, the further analysis on the desorption study was done based on the Freundlich desorption isotherm.

Table 4.11: The parameters for Freundlich desorption isotherm.

Sample	Log $K_{f\ des}$	$K_{f\ des}$	$1/n_{\ des}$	R^2
322	-0.6629	0.217320152	1.2549	0.9804
327	-1.074	0.084333476	1.9355	0.9953
328	-0.6254	0.23691906	1.0248	0.9059
X-mining	-2.5767	0.00265033	2.5507	1

Based on the Freundlich desorption isotherm obtained, the correlation coefficient was significant with R^2 value within range of 0.9 to 1.0. The highest desorption rate was the sample with the lowest $K_{f\ des}$ because the isotherm was calculated based on the mass of Imazapyr that been adsorbed by the soil. It was the same as the calculation used in Freundlich desorption isotherm. The arrangement of desorption rate of the soil samples started with the highest was X-mining>327>322>328. The X-mining soil had the highest desorption rate with 0.003 while Soil 328 had the lowest desorption rate with 0.24. X-mining soil was a sandy soil with high soil pH value and absent of clay content in its texture. Due to absent of clay content, X-mining soil could not bind the Imazapyr molecules stronger and longer compare to the other soil. Thus, the Imazapyr molecules desorbed easily from the X-mining soil particles.

The $1/n_{des}$ obtained was within the range of 1.02 to 2.55 which was greater than 1. Thus, the desorption isotherm obtained was linear which indicate that the amount of Imazapyr adsorbed was easily desorbed by the soil.

According to Wu (2011), there was a need to find hysteresis coefficient between adsorption and desorption isotherm. The hysteresis calculation was using the following equation:

$$H = \frac{\frac{1}{n}des}{\frac{1}{n}ads}$$

$1/n_{des}$ and $1/n_{ads}$ – obtained from the linear Freundlich adsorption-desorption isotherm.

Table 4.5 shows the hysteresis coefficient value for all the soil samples.

Table 4.12: The hysteresis coefficient value for all the soil samples based on Freundlich sorption isotherm.

Sample	$1/n_{ads}$	$1/n_{des}$	H
322	0.9027	1.2549	1.390163
327	0.887	1.9355	2.182074
328	0.8616	1.0248	1.189415
X-mining	0.9117	2.5507	2.79774

According to Wu (2011), the hysteresis coefficient, *H*, value of 1 means that desorption proceeds as fast as adsorption and no hysteresis occurs. A value of $H < 1$ indicates that the rate of desorption is slower than the rate of adsorption and hysteresis occurs. Meanwhile, a value of $H>1$ indicates the rate of desorption is faster than rate of adsorption.

Based on the hysteresis coefficient values obtained, the H values were within range of 1.19 to 2.80, which was greater than 1. This hysteresis value indicated that the desorption process occur faster than the adsorption process. This was probably happen due to the all soil samples did not have sufficient organic carbon content to adsorb and hold Imazapyr molecules stronger and longer.

4.5 Correlation of Adsorption-desorption value with soil physical properties

A linear regression analyses between $K_{f\text{-ads}}$ and $K_{f\text{-des}}$ with selected soil properties were performed to determine the degree of influence of each soil characteristics on adsorption and desorption by statistical approximation.

Adsorption Study

For adsorption study, all of soil properties that been analyzed previously, had been selected for the linear regression analysis. The soil properties were soil pH, soil total organic carbon, clay content, maximum water holding capacity, and field capacity.

Soil pH

Figure 4.11 showed the linear regression of $K_{f\ ads}$ against soil pH.

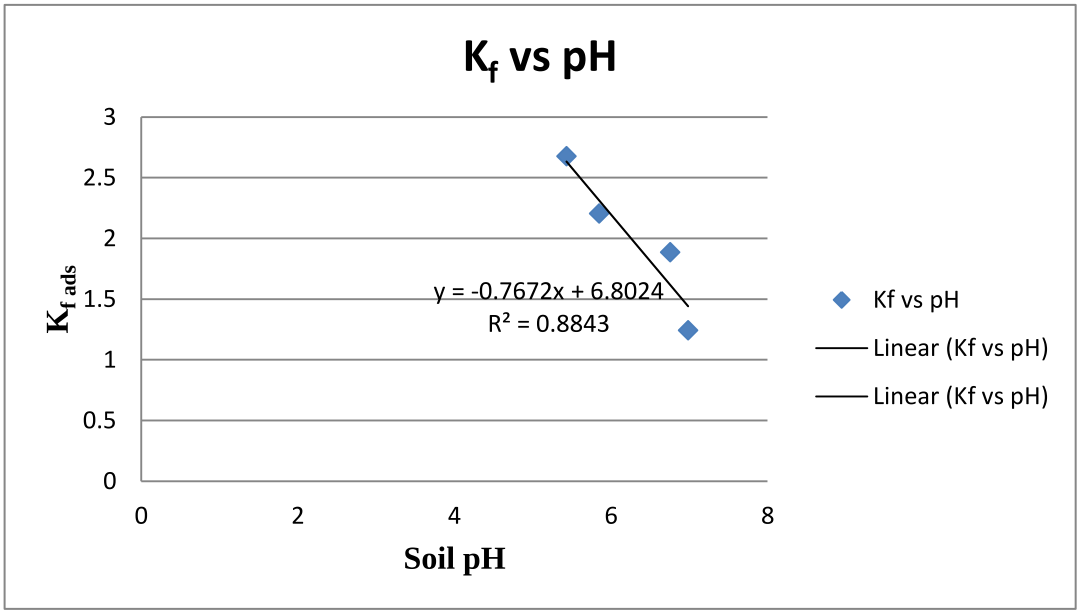


Figure 4.11: Linear regression of $K_{f\ ads}$ against soil pH.

Based on the linear regression of $K_{f\ ads}$ against soil pH, the relation observed was inversely proportional. As the pH increased, the adsorption rate decreased. The gradient of the linear regression was -0.7672. The correlation value, R^2 was significant with value of 0.8843.

Total Organic Carbon

Figure 4.12 showed the linear regression of $K_{f\ ads}$ against soil total organic carbon.

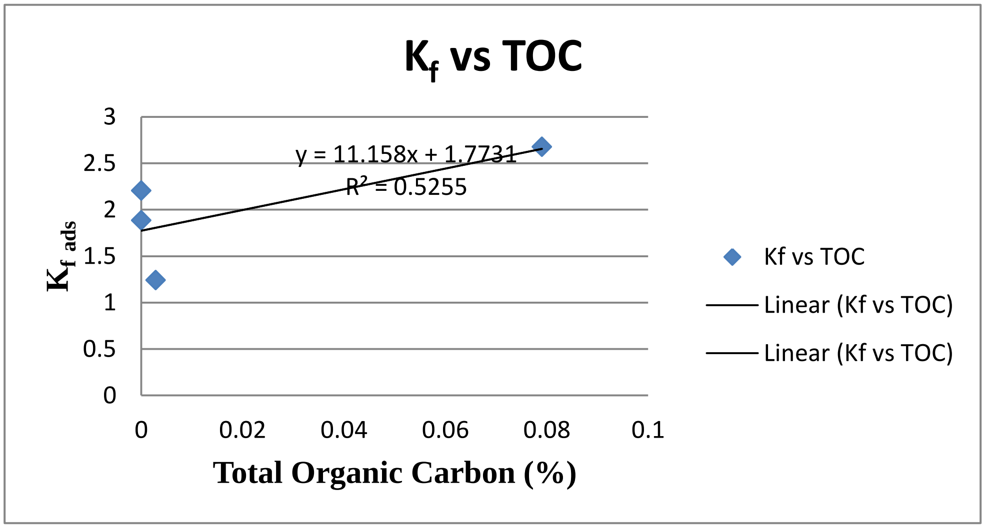


Figure 4.12: Linear regression of $K_{f\ ads}$ against soil total organic carbon.

Based on the linear regression of $K_{f\ ads}$ against soil total organic carbon, the relation observed was directly proportional. As the soil total organic carbon increased, the adsorption rate increased. The gradient of the linear regression was 11.158. The correlation value, R^2 was less significant with value of 0.5255.

Clay Content

Figure 4.13 showed the linear regression of $K_{f\ ads}$ against soil clay content.

Based on the linear regression of $K_{f\ ads}$ against soil clay content, the relation observed was directly proportional. As the soil clay content increased, the adsorption rate increased. The gradient of the linear regression was 0.0104. The correlation value, R^2 was not significant with value of 0.1772.

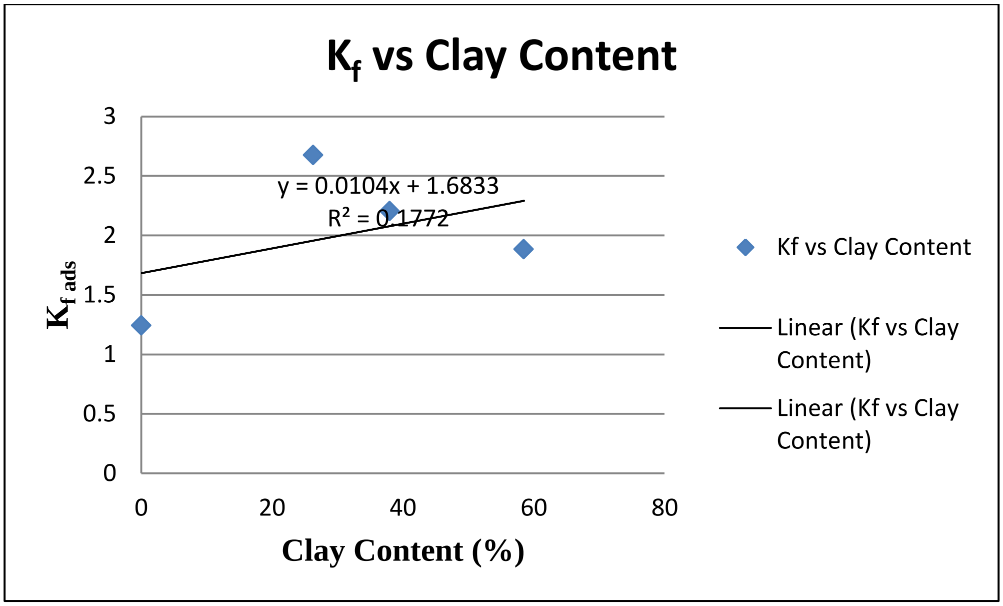


Figure 4.13: Linear regression of $K_{f\ ads}$ against soil clay content.

Maximum Water Holding Capacity and Field Capacity

Figure 4.14 showed the linear regression of $K_{f\ ads}$ against soil maximum water holding capacity.

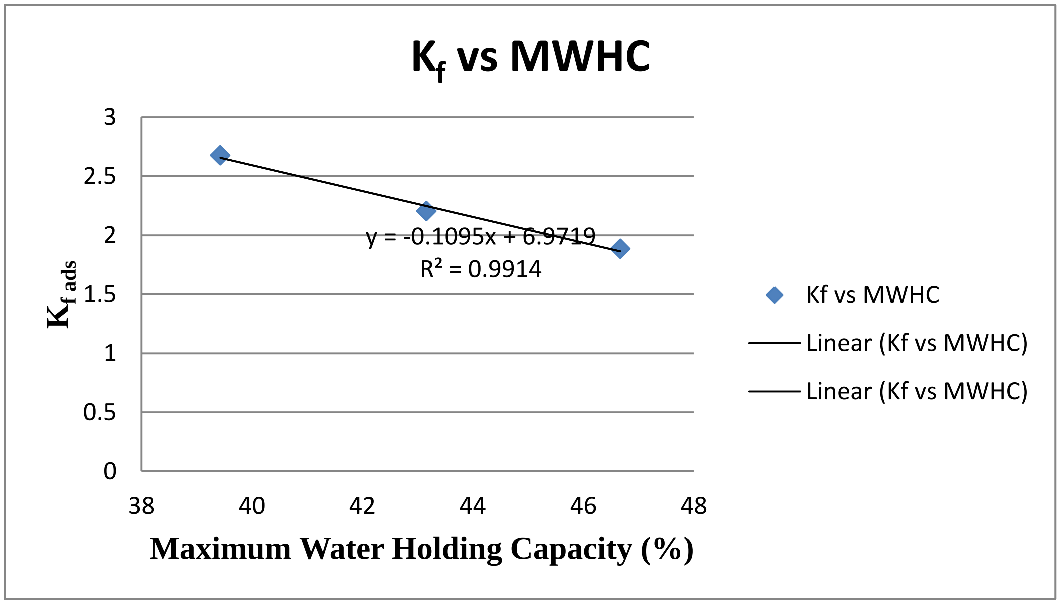


Figure 4.14: Linear regression of $K_{f\ ads}$ against maximum water holding capacity.

Based on the linear regression of $K_{f\ ads}$ against soil clay content, the relation observed was directly proportional. As the soil clay content increased, the adsorption rate increased. The gradient of the linear regression was -0.1095. The correlation value, R^2 was significant with value of 0.9914.

Figure 4.15 showed the linear regression of $K_{f\ ads}$ against soil field capacity.

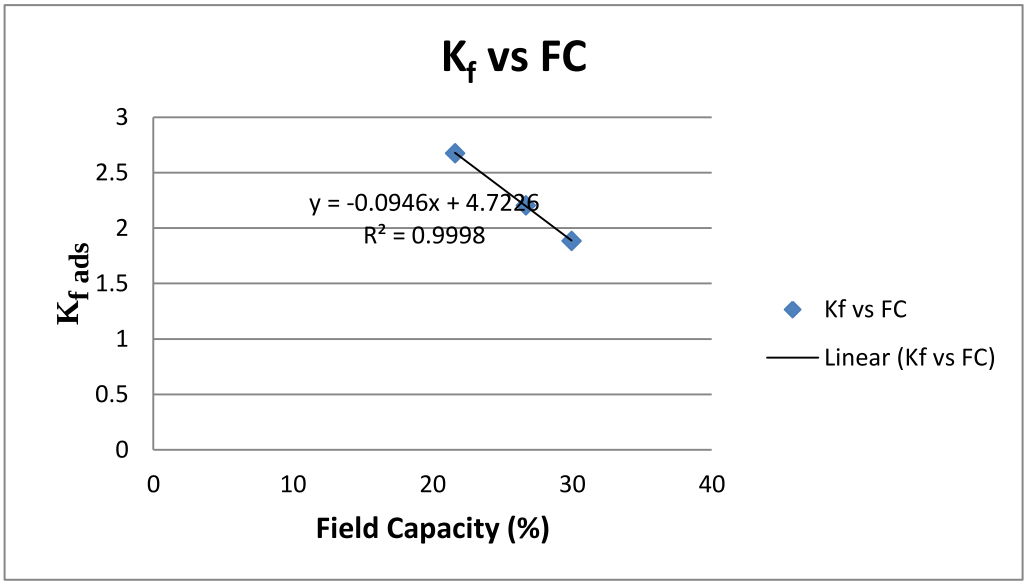


Figure 4.15: Linear regression of $K_{f\ ads}$ against field capacity.

Based on the linear regression of $K_{f\ ads}$ against soil clay content, the relation observed was directly proportional. As the soil clay content increased, the adsorption rate increased. The gradient of the linear regression was -0.0946. The correlation value, R^2 was significant with value of 0.9998.

Exchangeable Ca^{+2}, Mg^{+2}, Na^{+} and K^{+} and Cation Exchange Capacity (CEC)

Figure 4.16 showed the linear regression of $K_{f\ ads}$ against CEC.

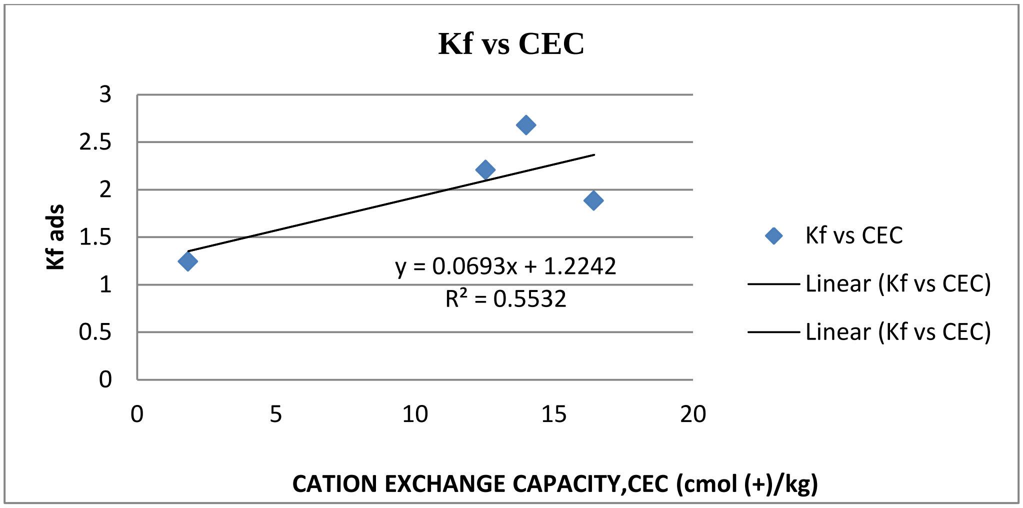


Figure 4.16: Linear regression of $K_{f\ ads}$ against CEC.

Based on the linear regression of $K_{f\ ads}$ against CEC, the relation observed was directly proportional. As the CEC increased, the adsorption rate increased. The gradient of the linear regression was 0.0693. The correlation value, R^2 was less significant with value of 0.5532.

Desorption Study

For desorption study, all of soil properties that been analyzed previously, had been selected for the linear regression analysis. The soil properties were soil pH, soil total organic carbon, clay content, maximum water holding capacity, and field capacity.

Soil pH

Figure 4.17 shows the linear regression of $K_{f\ des}$ against soil pH.

Based on the linear regression of $K_{f\ des}$ against soil pH, the relation observed was inversely proportional. As the soil pH increased, the desorption rate decreased. The gradient of the linear regression was -0.0568. The correlation value, R^2 was not significant with value of 0.1409.

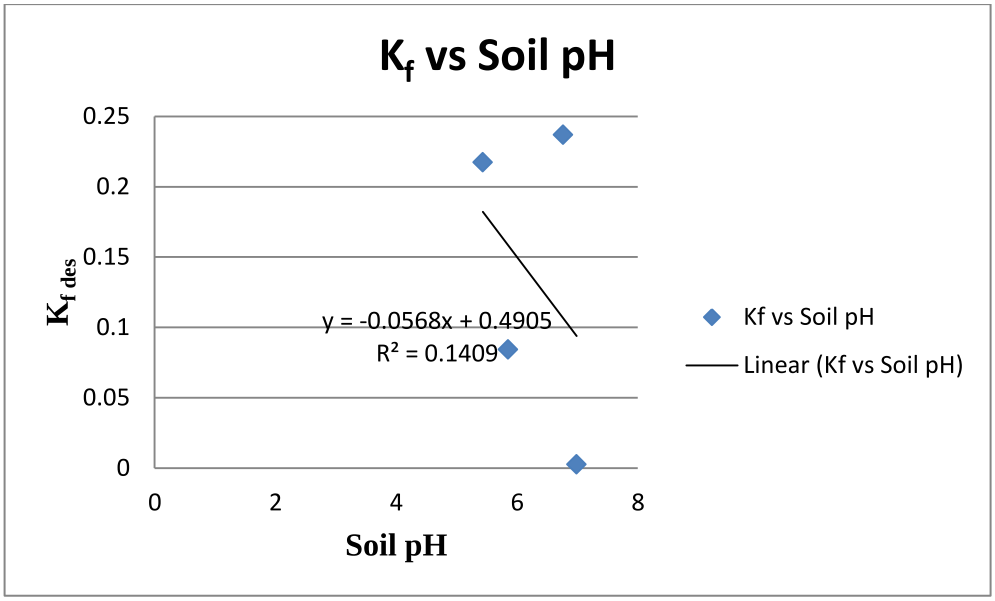


Figure 4.17: Linear regression of $K_{f\ des}$ against soil pH.

Total Organic Carbon

Figure 4.18 showed the linear regression of $K_{f\ des}$ against soil total organic carbon content.

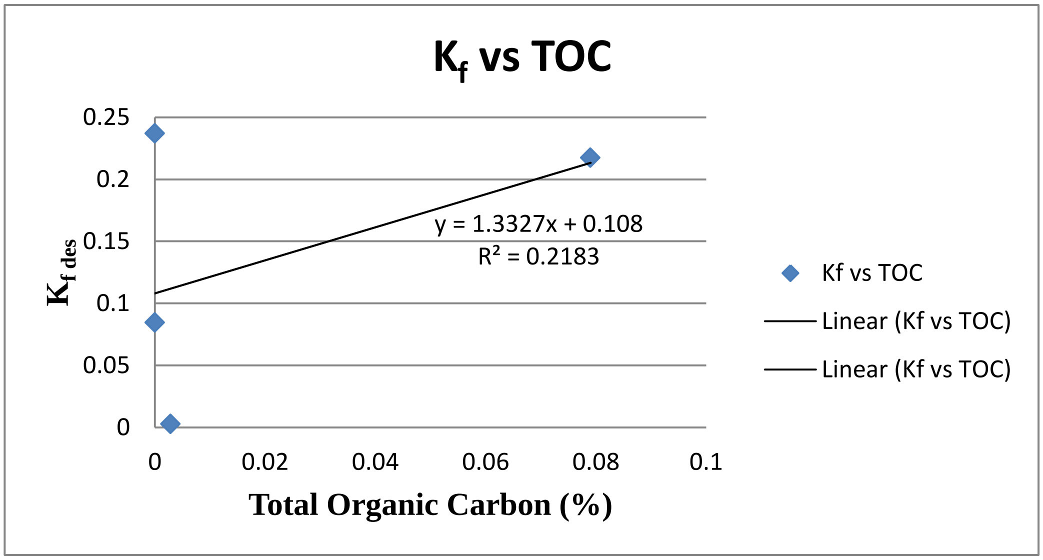


Figure 4.18: Linear regression of $K_{f\ des}$ against soil total organic carbon content.

Based on the linear regression of $K_{f\ des}$ against soil total organic carbon content, the relation observed was directly proportional. As the soil clay content increased, the desorption rate increased. The gradient of the linear regression was 1.3327. The correlation value, R^2 was not significant with value of 0.2183.

Clay Content

Figure 4.19 showed the linear regression of $K_{f\ des}$ against soil clay content.

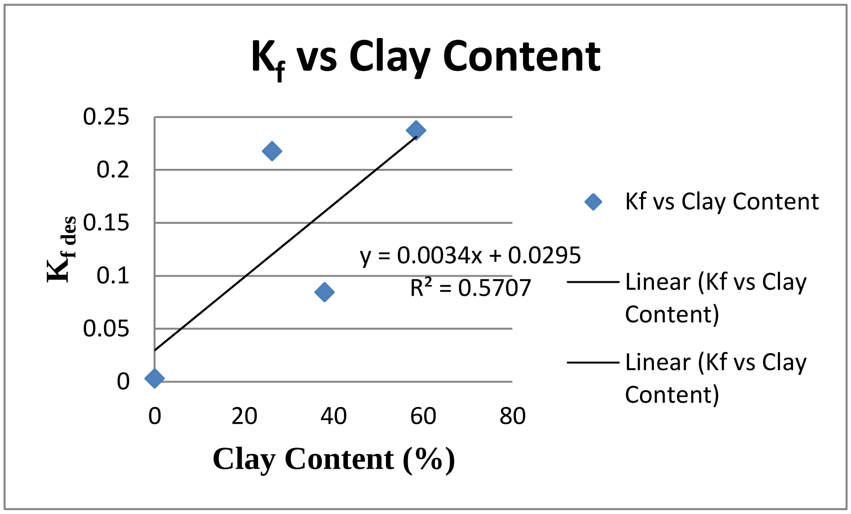


Figure 4.19: Linear regression of $K_{f\ des}$ against soil clay content.

Based on the linear regression of $K_{f\ des}$ against soil clay content, the relation observed was directly proportional. As the soil clay content increased, the adsorption rate increased. The gradient of the linear regression was 0.0034. The correlation value, R^2 was less significant with value of 0.5707.

Maximum water holding capacity and field capacity

Figure 4.20 showed the linear regression of $K_{f\ des}$ against soil maximum water holding capacity.

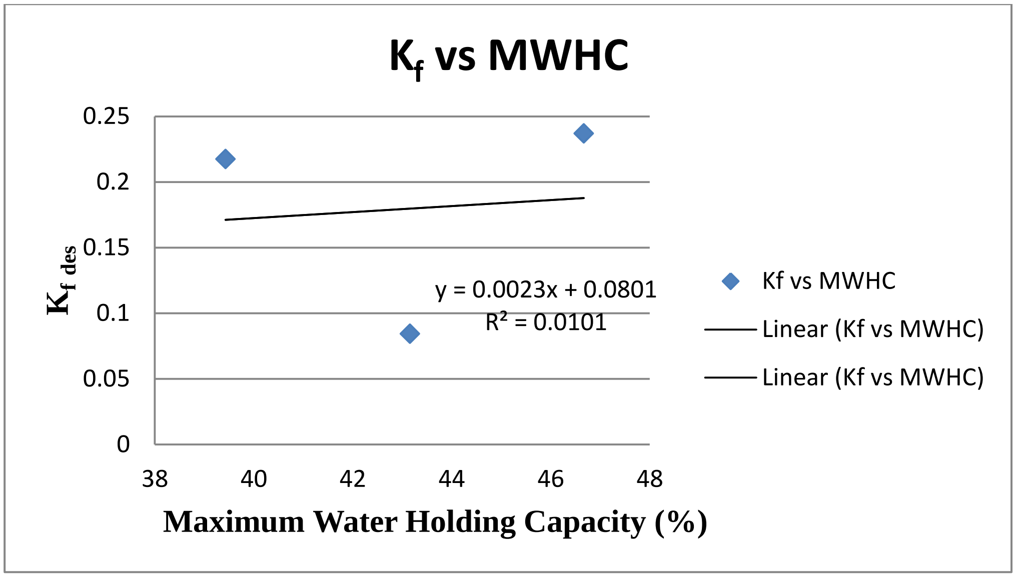


Figure 4.20: Linear regression of $K_{f\ des}$ against maximum water holding capacity.

Based on the linear regression of $K_{f\ des}$ against maximum water holding capacity, the relation observed was directly proportional. As the soil clay content increased, the adsorption rate increased. The gradient of the linear regression was 0.0023. The correlation value, R^2 was not significant with value of 0.0101.

Figure 4.21 showed the linear regression of $K_{f\ des}$ against soil field capacity.

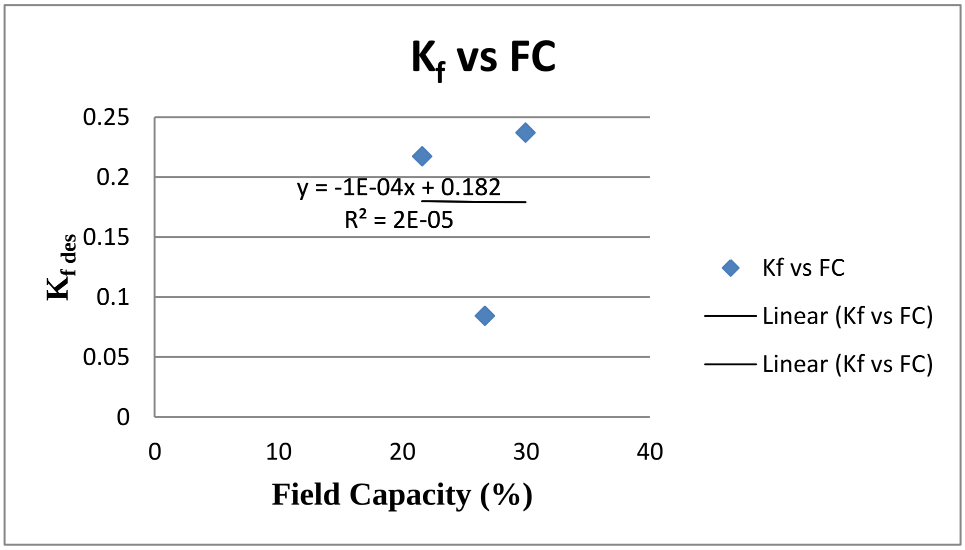


Figure 4.21: Linear regression of $K_{f\ des}$ against field capacity.

Based on the linear regression of $K_{f\ des}$ against field capacity.The relation observed was inversely proportional. As the field capacity increased, the desorption rate decreased. The gradient of the linear regression was -0.0001. The correlation value, R^2 was not significant with value of 0.00002.

Exchangeable Ca^{+2}, Mg^{+2}, Na^+ and K^+ and Cation Exchange Capacity (CEC)

Figure 4.22 showed the linear regression of $K_{f\ des}$ against CEC.

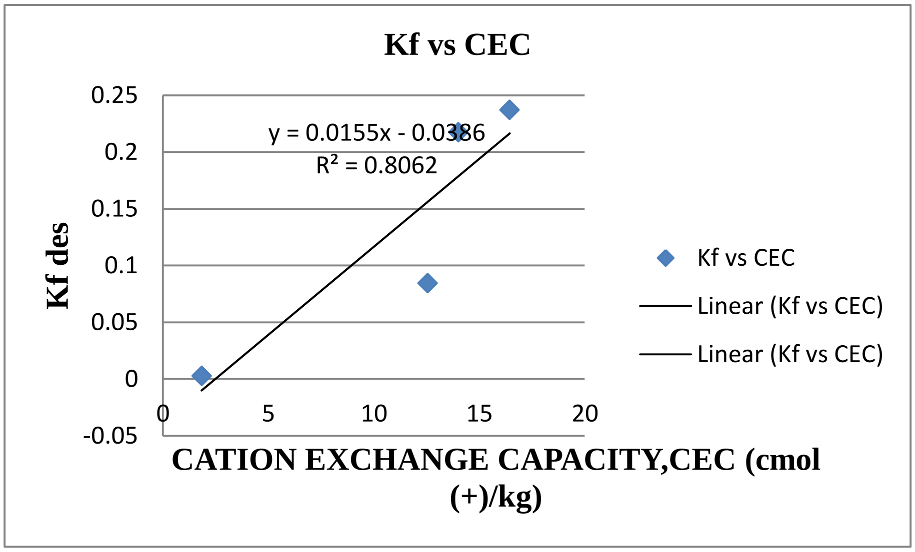


Figure 4.22: Linear regression of $K_{f\ des}$ against CEC.

Based on the linear regression of $K_{f\ des}$ against CEC, the relation observed was directly proportional. As the CEC increased, the desorption rate increased. The gradient of the linear regression was 0.0155. The correlation value, R^2 was not significant with value of 0.8062.

Table 4.13 showed the equation and R^2 of correlation between adsorption-desorption coefficient with the soil properties.

Table 4.13: Equation and R^2 of correlation between adsorption-desorption coefficient .with the soil properties.

Soil Parameters	Adsorption		Desorption	
	Equation	R^2	Equation	R^2
Soil pH	y = -0.7672x + 6.8024	0.8843	y = -0.0568x + 0.4905	0.1409
Total Organic Carbon, TOC (%)	y = 11.158x + 1.7731	0.5255	y = 1.3327x + 0.108	0.2183
Clay Content (%)	y = 0.0104x + 1.6833	0.1772	y = 0.0034x + 0.0295	0.5707
Maximum Water Holding Capacity (%)	y = -0.1095x + 6.9719	0.9914	y = 0.0023x + 0.0801	0.0101
Field Capacity (%)	y = -0.0946x + 4.7226	0.9998	y = -1E-04x + 0.182	2.00E-05
CEC (cmol (+)/kg)	y = 0.0693x + 1.2242	0.5532	y = 0.0155x - 0.0386	0.8062

For adsorption study, the correlation coefficient, R^2 for adsorption obtained was within the range of 0.177 to 0.9998 and the values were quite significant. The $K_{f\text{-}ads}$ seems to have higher correlation with soil pH, maximum water holding capacity and field capacity. The R^2 value for $K_{f\text{-}ads}$ with field capacity was the highest with 0.9998, followed by water holding capacity with 0.9914 and lastly by soil pH with 0.8843. For total organic carbon and clay content, the R^2 values were lower with 0.5255 and 0.1772 respectively. It shown that Imazapyr adsorption process was much affected by maximum water holding capacity, field capacity and soil pH compare to the total organic carbon and clay content.

Furthermore, the relation between $K_{f\text{-}ads}$ with soil pH, water holding capacity and field capacity were found to be inversely proportional based the equation's slope obtained. Thus, the adsorption occurred was decreasing as the soil pH, maximum water holding capacity, and field capacity was increasing. Otherwise, for total organic carbon content and clay content, the relation was directly proportional. As total organic carbon and clay content were increasing, the adsorption rate was also increasing. The same relation was found by Gianelli (2014), Kah (2007) and Pusino (1997). According to Johnson (1987), imidazolinone herbicides tend to be more adsorbed under acidic or low soil pH which reduces their availability for microbial degradation.

High maximum water holding capacity and field capacity did increase the soil moisture content. The moisture holding capacity of soils made the Imazapyr conducive for increased microbial activity (Johnson, 1987). Since Imazapyr was soluble in water, the increased soil moisture could lead the declination of Imazapyr molecules available for adsorption process. Pesticides with water solubility of less than 1 ppm tend to remain on the soil surface. They tend not to be leached, but may move with soil sediment in surface runoff if soil erosion occurs. Pesticides with water solubility greater than 30 ppm are more likely to move with water.

Moreover, the adsorption rate increased as the soil pH decreased. The pH dependence of sorption derives mainly from the different proportions of ionic and neutral forms of the herbicide at each pH level and from differences in its strength of sorption .Thus, depending on pH, imazapyr can exist in cationic, neutral, and anionic forms. Imazapyr exhibits different adsorption behaviors depending on the soil pH. Over the measurable pH range, the herbicide exhibits two protonation sites, the carboxylate group and the pyridine-type nitrogen of the imidazolinone ring, which dissociate with p*K*a values of 3.6 and 1.9, respectively. Instead, the lactam group dissociates in water with p*K*a 10.8. Thus, imazapyr can exist in cationic, neutral, and anionic forms depending on soil pH. The cationic, neutral and anionic forms of Imazapyr are shown in **Figure 4.22**. However, in the pH range 5.43-6.99 examined in this study, only the anionic form of imazapyr is available in solution.

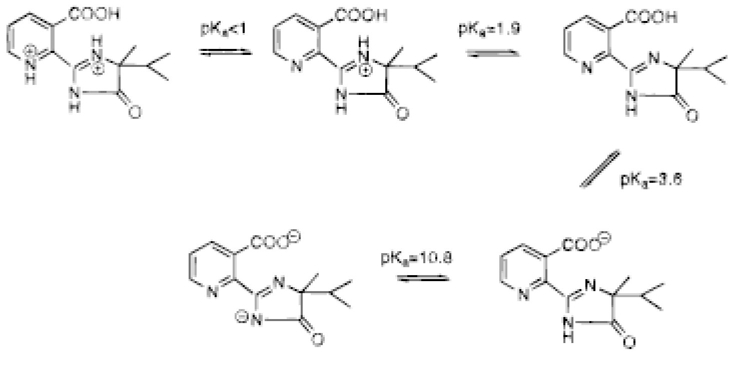


Figure 4.23: Cationic, neutral and anionic forms of Imazapyr

The repulsion of the anionic molecule with the negatively charged surfaces explains why the organic matter promotes imazapyr adsorption only in the soils with rather low pH values. The anionic form of imazapyr predominates from pH 5 to pH 9. In this form, Imazapyr molecules were weakly bound or repulsed by negative charges of soil colloids, resulting in low sorption to neutral and high pH soils. As the pH of the soil decreases, the neutral and cationic forms were increasing, thus, increased soil sorption and changed soil surface ionic charge because of pH amplifying the sorption effect (Gianelli, 2014).

For desorption study, the correlation coefficient, R^2 for desorption obtained was within the range of 0.00002 to 0.806 and the values were less significant. The $K_{f\text{-}des}$ seems to have higher correlation with CEC and clay content. The R^2 value for $K_{f\text{-}des}$ with CEC was the highest with 0.8062, followed by clay content with 0.5707, then by total organic carbon with 0.2183 and lastly by soil pH with 0.1409. For maximum water holding capacity and field capacity, the R^2 values were lower with 0.0101 and 0.00002 respectively. It shown that Imazapyr adsorption process was much affected by the CEC and clay content compare to other soil properties which were total organic carbon, clay content, soil pH, maximum water holding capacity and field capacity.

The relation between $K_{f\ des}$ with CEC, total organic carbon, clay content, and maximum water holding capacity were found to be inversely proportional. As the CEC, total organic carbon, clay content and maximum water holding capacity increased, the desorption rate decreased. Meanwhile, the relation between $K_{f\ des}$ with soil pH and field capacity was found to be directly proportional. Thus, as the soil pH and field capacity increased, the desorption rate increased.

As the CEC, total organic carbon and clay content increased, the soil particles could hold the Imazapyr molecules longer and stronger, thus, the molecules were difficult to desorb from the soil. Thus desorption of Imazapyr might be mostly attributed to the effect of CEC, total organic carbon and clay content.

CHAPTER 5

CONCLUSION

In conclusion, the results indicate that it is a rather difficult task to state what soil component is effective in imazapyr adsorption by soil. However, it can be supposed that depending on soil pH, the organic carbon content, clay content, maximum water holding capacity and field capacity may be effective in the process. Both adsorption and desorption data fit well with Freundlich sorption isotherm. Further studies are necessary to clarify the kind of binding mechanisms acting in imazapyr adsorption on soil.

Furthermore, the most significant factors that affect the adsorption of Imazapyr are maximum water holding capacity, field capacity and soil pH. As the maximum water holding capacity, field capacity and soil pH are lower, the adsorption rate increased. It is an inversely proportional relation between adsorption rate and maximum water holding capacity, field capacity and soil pH factors.

Moreover, the most significant factors that affect the desorption of Imazapyr are clay content and organic carbon content. As the clay content and organic carbon content are higher, the desorption rate increased. It is a directly proportional relation between adsorption rate and the clay content and organic carbon factors.

CHAPTER 6

RECOMMENDATION

This study need to be furthered researched in the future. It is much related with the current environmental condition in Malaysia regarding the application of herbicide in paddy field. It is expected that the On Duty herbicide will be commercialize to around the country in the near future. So, precaution steps need to be planned since now to reduce the environmental impact of the herbicide.

It is recommended to study the adsorption and desorption of Imazapic, the other Imidazolinone applied in On-duty herbicide. Imazapic has different characteristics with Imazapyr. Thus, by having both adsorption and desorption studies of On Duty herbicides, the precaution and mitigation measures can be done effectively.

For experimental purposes, it is suggested the future study to be done better in term of number of samples and the number of soil analysis experiments. Both aspects need to be increased in quantity.

CHAPTER 7

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