ABSTRACTION OF TEBUCONAZOLE AND CLOMAZONE PESTICIDE RESIDUES FROM WATER BY ZEOLITE X: KINETICS AND THERMODYNAMICS STUDIES

BY

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ABSTRACT

The presence of pesticide residues in water sources is of great environmental concern due to the detrimental health problems to human and organisms in the aquatic environment associated with pesticide toxicities. Among the widely used pesticides are tebuconazole and clomazone, used in cultivation of numerous crops. Tebuconazole and clomazone have been detected in rivers, streams and lakes at levels exceeding the set safe allowable limits for drinking water. Conventional water treatment technologies that use activated carbon singly have been demonstrated to be insufficient in pesticide removal from wastewater. There is therefore need to evaluate other adsorbents for pesticide remediation from water. Synthetic sodium-type faujasite X (NaX) has been reported to have the capacity to abstract pesticides residues from water. However, the potential of NaX to adsorb tebuconazole and clomazone has not been documented. The objective of this study was to investigate the adsorption behavior of tebuconazole and clomazone pesticides from aqueous solution onto NaX. The effects of pesticide concentration (100 - 1000 μg L^{-1}), contact time (15 - 390 min) and temperature (293 - 323 K) on the adsorption process were investigated using batch shaking sorption experiments using HPLC-DAD and the site of adsorption identified by FT-IR and XRD techniques. Removal efficiency varied significantly ($p<0.05$) with the initial pesticide concentration for both pesticides. Langmuir and Freundlich models gave the best fit for the experimental data for both pesticides. The maximum adsorption capacity of tebuconazole onto NaX, calculated from Langmuir isotherm, was 500 μg g^{-1}. The adsorption reaction was found to follow pseudo-second order kinetics for both pesticides. The sorption half-life was evaluated and the adsorption rate of tebuconazole (0.0634 h) was faster than that of clomazone (0.1177 h). The calculated thermodynamic parameters indicate that tebuconazole adsorption on NaX is spontaneous ($\Delta G=-180.7$ J $mole^{-1}$) and exothermic ($\Delta H=-38.7$ kJ $mole^{-1}$) while clomazone adsorption was non-spontaneous ($\Delta G=5719.6$ J $mole^{-1}$) and exothermic ($\Delta H=-44.9$ kJ $mole^{-1}$) under the examined conditions. Intraparticle diffusion model showed that the adsorption of tebuconazole and clomazone onto NaX was multi-mechanistic and was not controlled by pore diffusion. FT-IR and XRD analysis indicated that adsorption of tebuconazole and clomazone onto NaX is an external surface chemisorption process at the single-four-rings (S4R) of the zeolite framework with involvement of the Na^+ cations. The results show that NaX is a better adsorbent for tebuconazole removal than clomazone and is valuable for wastewater treatment plants for tebuconazole remediation.

CHAPTER ONE

INTRODUCTION

1.1 Background

Pesticides are widely used to boost agricultural production and to reduce post harvest losses (Pareja *et al*., 2011). Among the widely used pesticides are tebuconazole and clomazone; which are used in cultivation of different crops including maize, vegetable crops, and cereals as fungicides and herbicides, respectively (Fenoll *et al*., 2009; Zanella *et al*., 2002). However, due to uncontrolled and at times abusive use, these pesticides and their respective degradation products, find their way into rivers, lakes and ground water by leaching, uncontrolled dumping of agrochemical refuse, release of untreated industrial effluents, surface run-off, sewer overflows, leaking of faulty equipments and farmyard deposition (Foo and Hameed, 2009; Reichenberger *et al*., 2007) resulting to deterioration of water quality endangering indigenous ecologies, fauna, flora and environmental matrix (Gentz, 2009). Tebuconazole and clomazone have been detected in wastewater and rivers at levels exceeding the EU's set allowable limit of 0.1 $\mu g\ L^{-1}$ for drinking water (Elsaesser and Schulz, 2008; Mattice *et al*., 2010). Both tebuconazole and clomazone are known to be toxic to aquatic organisms, animals and humans and may cause long-term diverse effects in aquatic environment (Yu *et al*., 2013; Quayle *et al*., 2006). Due to their toxicity, the environmental fate of tebuconazole and clomazone is of great concern. However, work on remediation of these pesticides from contaminated waters is scanty.

Conventional wastewater treatment methods, which mainly use activated carbon singly, have been demonstrated to be insufficient in removal of most pesticides and their residues yet they are widely used in most developing countries (Mathur *et al*., 2003; MSUE, 2003). There is therefore need for development of effective and sustainable alternative remedial strategies for pesticide removal from wastewaters.

Faujasite X in the Na^+ form has the capacity to abstract and enhance degradation of malathion and organochloride pesticides in water (Ogunah *et al*., 2013; Kowenje *et al*., 2013; Patterson *et al*., 2006). Agoro *et al*. (2013) also showed that NaX can both adsorb and chemically degrade triazine herbicide, hexazinone. The role of NaX in converting hazardous wastes into environmentally friendly products less toxic than the parent molecule has also been demonstrated by Kowenje *et al*. (2013) and can thus be used to purify agricultural wastewater before discharge to other recipient water bodies or in case of a major spillage. Though the studies report the kinetics and interaction mechanisms of the pesticides and NaX, the studies did not report the thermodynamic characteristics of the reactions and isothermal behavior of the adsorption processes. Sorption studies have shown that zeolites adsorb pesticide molecules on their interior and exterior surfaces or in their pore openings of fixed and uniform dimension (Yang *et al.*, 2006) and thus significantly reduces the pesticide concentration in water by acting as molecular sieves (Jonan *et al.*, 2006). However, the adsorption behavior by sodium type faujasite X (NaX) has not been reported for tebuconazole and clomazone pesticides in water. The current study therefore investigated the potential of using sodium-type faujasite X as an end of line adsorbent for removal of tebuconazole and clomazone pesticide residues from water.

1.2 Problem statement

Tebuconazole and clomazone are widely used in agricultural areas to optimize crop yields. The residues of these pesticides eventually end up as contaminants of water resources. Exposure of end users and non-target organisms in the environment to the pesticide residues and their degradation products poses detrimental risks to their health and existence. The current strategies for agricultural wastewater treatment that mainly employ activated carbons singly are not sufficient in removal of most pesticides from water; hence delivery of safe drinking water still remains a great challenge. This study evaluated the efficacy of Na^+ type faujasite X in removing tebuconazole and clomazone pesticide residues from water as a possible alternative wastewater treatment technique.

1.3 Hypothesis

1.3.1 Null hypothesis

Faujasite X (NaX) cannot significantly adsorb tebuconazole and clomazone residues from water.

1.4 Objective of study

To determine the kinetics and thermodynamics for adsorption behaviour of tebuconazole and clomazone in water onto synthetic sodium-type faujasite X (NaX) and evaluate the adsorption efficiency of the zeolite in removal of these pesticides from water as a potential adsorbent for agricultural wastewater treatment.

1.5 Specific objectives

1. To determine the effect of initial pesticide concentration on the adsorption extent of tebuconazole, and clomazone onto faujasite X.
2. To determine the operational adsorption isotherm parameters for aqueous tebuconazole, and clomazone onto faujasite X.
3. To determine the thermodynamic parameters of the pesticides dissipation in water in the presence of the faujasite X.
4. To determine the adsorption kinetics and infer the adsorption mechanism of tebuconazole, and clomazone onto faujasite X.
5. To identify the site of adsorption of tebuconazole and clomazone on the zeolite framework.

1.6 Justification of the study

Tebuconazole and clomazone have detrimental effects on aquatic life, animals and human beings (Yu *et al.*, 2013; USEPA, 2006; Quayle *et al.*, 2006). Since these pesticides find their way into the environment through anthropogenic paths, leaching and surface run-offs, ground water and other water sources are vulnerable to pesticide contamination (Kahle *et al.*, 2008; Mervosh *et al.*, 1995) posing a health risk to the ecosystem. Current strategies for remediation of their residues from water are insufficient and non-specific while better alternative technologies are costly for developing countries. There is therefore a need to develop efficient and sustainable technologies for wastewater treatment with respect to tebuconazole and clomazone residues.

NaX has been demonstrated to have the capacity to adsorb and enhance chemical degradation of organophosphate and organochloride insecticides and triazine herbicides pesticides in water into less toxic degradation products (Kanyi *et al.*, 2006; Kowenje *et al.*, 2013). However, data on adsorption of triazole fungicides and isoxazolidinone herbicides onto NaX is lacking. Synthetic zeolites, such as faujasite X, have known and controlled structures and can be regenerated after use (Damjanovic *et al.*, 2010). This property gives them the potential of being efficient and sustainable alternatives in pesticide remediation from water and accelerators of pesticide degradation. Therefore the faujasite X may go a long way in solving the problem at hand.

CHAPTER TWO

LITERATURE REVIEW

2.1 Pesticide use

The steady increase in world population over the years has put pressure on food security and supply (Carvalho, 2006). This population increase over the years has led to intensification of agricultural practices and increased use of pesticides to optimize crop yields and reduce post harvest losses (Pareja *et al.*, 2011) to meet the increasing food production demand. The use of pesticides, in the form of herbicides, insecticides, fungicides, algaecides, antimicrobials, nematocides, bactericides, molluscicides among others, has led to pollution, especially of surface and ground water resources, which has become one of the leading environmental concerns worldwide. These toxic compounds find their way into water sources either through leaching, uncontrolled dumping of agrochemical refuse, release of untreated industrial effluents, surface run-off, sewer overflows, leaking of faulty equipments and farmyard deposition (Foo and Hameed, 2009; Reichenberger *et al.*, 2007) resulting to deterioration of water quality endangering indigenous ecologies, fauna, flora and environmental matrix (Gentz, 2009).

Continual exposure to these pesticides and their metabolites through use of contaminated waters has been reported to be detrimental to human health. Such conditions include cancerous tumors, birth defects and other developmental disorders which may be permanent (Waring and Harris, 2011; Anway *et al.*, 2005) especially in developing countries where level of healthcare is relatively low. Among the widely used pesticides are tebuconazole and clomazone (Rial-Otero *et al.*, 2005; Zanella *et al.*, 2002).

2.2 Tebuconazole

Tebuconazole, ((RS)-1-p-chlorophenyl-4,4-dimethyl-3-(1H-1,2,4triazol-1-ylmethyl) pentan-3-ol), is a triazole fungicide widely used in agriculture for crop protection. Triazoles are a class of fungicides whose antifungal activity is due to their capacity to inhibit the P450 enzyme which blocks the conversion of lanosteron to ergosteron causing disruption of fungal wall (Di Renzo *et al.*, 2007) while other triazoles have been reported as endocrine disruptors (Liu *et al.*, 2011, Mnif *et al.*, 2011). Due to its broad spectrum antifungal activities (Liu *et al.*, 2011; Mnif *et al.*, 2011), tebuconazole is widely used in controlling numerous pathogens in different crops including maize, vegetable crops, grapevines and cereals (Fenoll *et al.*, 2009; Rial-Otero *et al.*, 2005).

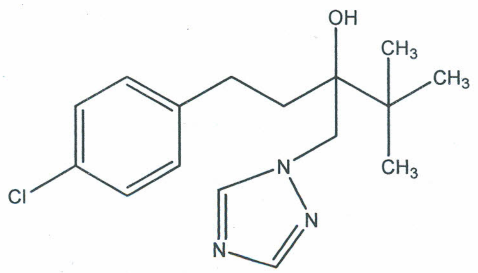

Figure 1: Structure of tebuconazole

Tebuconazole is classified as group C-possible human carcinogen (U.S EPA, 2006). It has been reported to be toxic to aquatic organisms and may cause long-term diverse effects on other organisms within the aquatic environment (Yu *et al.*, 2013). The physicochemical properties of tebuconazole are listed in Table 1.

Table 1. Physicochemical data for tebuconazole (Tomlin, 2003)

CAS RN	107534-96-3
Chemical formula	$C_{16}H_{22}ClN_3O$
Molecular mass (g mol^{-1})	307.82
Solubility - In water at 20°C (mg L^{-1})	36
Bulk density (g mL^{-1})	1.25
Aqueous hydrolysis DT50 (days) at 20°C and pH 7	Stable pH 5 to pH 9, at 25 °C, 28 days

2.2.1 Environmental fate of Tebuconazole

The dissipation behavior of any pesticide is an important indicator for assessing the environmental fate and possible residues that may cause detrimental harm to both human and non-target organisms. Tebuconazole is highly adsorbed in soils and presents higher degradation rates under field conditions compared to laboratory tests (EFSA, 2008). The rate of degradation is dependent on the soil organic carbon among other soil properties. The degradation of tebuconazole in soils under laboratory conditions has been studied by a number of researchers including White *et al.* (2010); Bending *et al.* (2007) and Potter *et al.* (2005). The half-life value for tebuconazole in soils ranges between 19-28 days depending on the dosage (Patyal *et al.*, 2013) and may pose a risk for ground water contamination. Tebuconazole has been detected in wastewater and lakes at levels exceeding the set allowable limits, with concentrations of up to 175-200 μg L^{-1} in surface waters (Elsaesser and Schulz, 2008; Kahle *et al.*, 2008; Berenzen *et al.*, 2005) and up to 19.2 μg L^{-1} in urine samples of agricultural workers (Fustinoni *et al.*, 2012). The presence of tebuconazole in stream waters has been shown to be on the increase in recent years (Montuelle *et al.*, 2010). Due to its toxicity, the environmental fate of tebuconazole is of great concern. However sufficient remediation of tebuconazole residues from contaminated waters is yet to be reported.

2.3 Clomazone

Clomazone, (2-[(2-chlorophenyl)methyl]-4,4-di- methyl-3-isoxazolidinone) belongs to a class of isoxazolidinone post-emergent herbicides widely used to control annual broadleaf weeds in the cultivation of soybeans, rice, sugar cane, tobacco, and a variety of other vegetable crops (Zanella *et al.*, 2002).

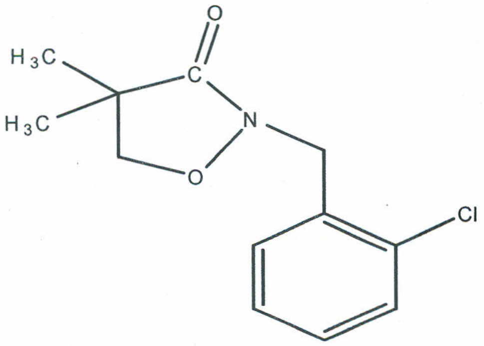

Figure 2: Structure of clomazone

Clomazone exposure is detrimental to aquatic life, leading to disorders in antioxidant parameters of the fish *Rhamdia quelen* (Menezes *et al.*, 2011). The physicochemical properties of tebuconazole are listed in Table 2.

Table 2. Physicochemical data for clomazone (Tomlin, 2003)

CAS RN	81777-89-1
Chemical formula	$C_{12}H_{14}ClNO_2$
Molecular mass (g mol^{-1})	239.7
Solubility - In water at 20°C (mg L^{-1})	1102
Bulk density (g mL^{-1})	1.19
Aqueous hydrolysis DT50 (days) at 20°C and pH 7	Stable pH 5 to pH 9, at 25 °C,

2.3.1 Environmental fate of Clomazone

Due to its high solubility (1100 μg L^{-1}) and a long half-life of 28-84 days, clomazone poses a high risk of ground water contamination (Mervosh *et al.*, 1995). Clomazone has been detected in surface waters at levels exceeding the E.U set allowable limit of 0.1 μg L^{-1} for drinking water (Mattice *et al.*, 2010). In soils, clomazone has been reported to degrade via both direct and indirect photolysis (Tomco and Tjeerdema, 2012). Due to its toxicity, several techniques have been proposed for clomazone remediation from wastewater. Among the most promising alternatives to activated carbon is the use of advanced oxidation processes (Chiron *et al.*, 2000) with the use of heterogeneous photocatalysis by TiO_2 appearing to be the most efficient method for elimination of clomazone from water (Abramovic *et al.*, 2013). However, photodegradation of pesticides is always accompanied by the formation of intermediates that can potentially be harmful to the environment (Chiron *et al.*, 2009); hence other environmentally friendly alternatives still need to be evaluated. Though many adsorbents have been reported for use in pesticide remediation from water, the literature is insufficient to cover this problem, and more studies are needed to develop suitable adsorbent for clomazone removal.

NaX has been shown to have the capacity to abstract and enhance chemical degradation of pesticides in water to less toxic residues than the parent molecule and can thus be used to purify agricultural wastewater before discharge to other recipient water bodies or in case of a major spillage (Ogunnah *et al.*, 2013). Compared to natural zeolites, synthetic zeolites are most utilized because of their controlled and known physico-chemical properties.

2.4 Zeolites

2.4.1 Zeolite structure

Zeolites are crystalline, hydrated aluminosilicates with a tetrahedral framework structure with channels and cages called micropores of fixed and uniform dimensions, containing exchangeable cations, allowing mass transfer from the exterior to the interior of the crystal (Jiang *et al.*, 2010). Depending on the dimensionality of the micropores, the zeolites are generally classified as small, medium and large pore size when the channels consists of eight, ten and twelve oxygen atoms, respectively (Jiang *et al.*, 2010). The general empirical formula of zeolite is given by:

$$M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot wH_2O$$

Where M denotes exchangeable cation of valence n, w is the number of water molecules per unit cell, while x and y represent the total number of tetrahedral molecules per unit cell (Gonghu, 2005). Of the large number of known zeolites, synthetic faujasite X, Figure 3, was of interest in the current study. This is due to its high Si/Al ratio which imbues it with high catalytic and adsorptive capability (Kowenje *et al.*, 2006; Ogunnah *et al.*, 2013).

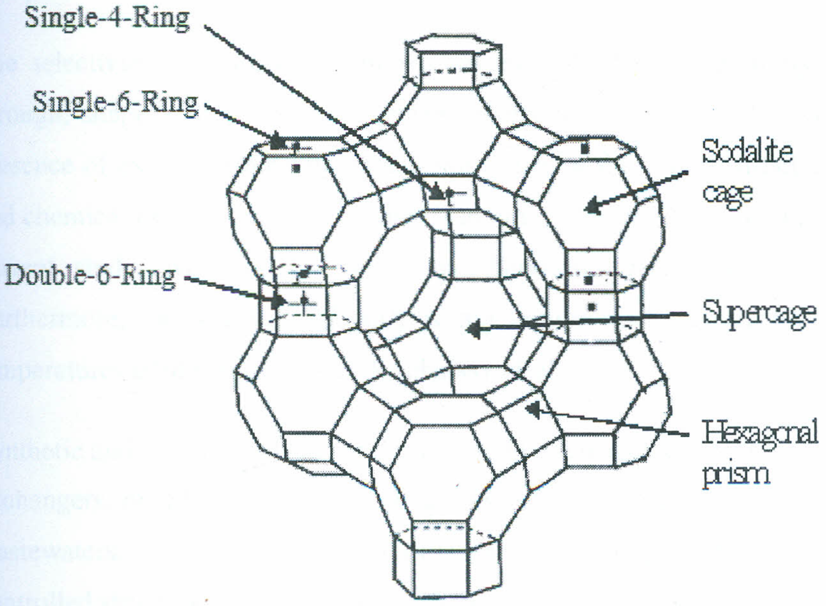

Figure 3. Structure of faujasite zeolite X (Nezamzadeh and Salimi, 2010)

The structure of sodium type faujasite X (NaX) has been described as consisting of tetrahedra linked together to form sodalite cage units of approximately 0.26 nm in size. The sodalite interconnections create a three dimensional structure with a twelve ring window of approximately 0.74 nm in diameter for a "supercage" of approximately 1.18 nm diameter with a Si/Al ratio of 1.23 (Kowenje *et al.*, 2006; Yang *et al.*, 2006).

2.4.2 Zeolite adsorption and catalysis of pesticides

Zeolites are of great interest in pesticide remediation due to their high adsorption capacities, catalytic chemical reactivity and the intrinsic capacity to be regenerated while maintaining their initial properties (Koubaissy *et al.*, 2008; Damjanovic *et al.*, 2010). They have the potential to adsorb on their interior and external surfaces and chemically decompose pesticides through nucleophilic reactions (Kanyi *et al.*, 2009; Yang *et al.*, 2006) to less toxic compounds than the parent molecule (Kowenje *et al.*, 2013).

The nucleophilic character of NaX is due to the delocalized negative charge between the "supercage" oxygen atoms and aluminium atoms which is stabilized by Na cations. Furthermore, the "supercage" cations also assist in the departure of anionic leaving groups (De Coste *et al.*, 2011).

The selectivity of adsorbates depends on the polarity, "reptatability"- ability to snake through, shape and size of the diffusing molecules relative to the zeolites opening; the presence of exchangeable cations and impurities in the zeolite structure and the physical and chemical tunability of the zeolite (Damjanovic *et al.*, 2010; Yonli *et al.*, 2012). In the current study, NaX was activated by thermally drying under vacuum conditions. Furthermore, the structure of NaX is not compromised under the vacuum and high temperatures used for activation (Koubaissy *et al.*, 2008).

Synthetic and natural zeolites have been used widely as adsorbent materials, catalysts, ion exchangers, membranes and molecular sieves for removal of various contaminants from wastewaters; however synthetic zeolites are preferred because they have known and controlled structures and composition compared to the natural zeolites.

Ogunnah *et al.* (2013) observes that sodium type faujasite X (NaX) reduces the half-life of malathion dissipation by half to less than 2.5 hours through a cation mediated mechanism. In the same study, removal of malathion is also attributed to adsorption. Faujasite X (NaX) efficacy to degrade malathion has also been reported by Patterson *et al.* (2006). Atrazine adsorption by zeolite X has been studied by Jamil *et al.* (2011) with adsorption being attributed to electrical attraction between the negative end of atrazine (chlorine atom) and the cations in the zeolite that act as localized charges. However, in the above mentioned studies, the thermodynamic properties of the process were not reported. The efficiency of NaX as adsorbent was also not evaluated at low pesticide concentrations, that is, near real environmental concentrations.

Sorption studies have shown that zeolites adsorb pesticide molecules in their pore openings of fixed and uniform dimension (Yonli *et al.*, 2012; Yang *et al.*, 2006) thus significantly reducing the pesticide concentration in water by acting as molecular sieves (Jonan *et al.*, 2006). The molecular sieving properties of zeolites are thus uniquely determined by their pore diameters, the magnitude of which determines what size molecules are totally excluded from the interior of the zeolite. Though sodium type faujasite X (NaX) has been shown to significantly reduce pesticide concentrations in water by abstraction and accelerated degradation (Kowenje *et al.*, 2013), its potential has not been reported for tebuconazole and clomazone pesticides removal from water.

2.5 Adsorption chemistry

Adsorption is the process of accumulating molecules that are in solution on a suitable interface. The adsorbate is the substance that is being removed from the liquid phase at the interface. The adsorbent is the solid, liquid or gas phase onto which the adsorbate accumulates. Therefore, adsorption involves the attachment of adsorbate to adsorbent at an available adsorption site (Metcalf and Eddy, 2003).

The term adsorption is also used to characterize the kind of forces of interaction between the adsorbate and the adsorbent. These interaction forces are broadly described as *physisorption* and *chemisorption* (Rouquerol, 1999). Physical adsorption (physisorption) is relatively non-specific and is due to the operation of weak inter-molecular forces. In this process, the adsorbed molecule is not affixed to a specific site on the solid surface but rather it is free to move over the adsorbent surface (Sawyer *et al.*, 1994). The physical interactions between molecules include electrostatic forces, dipole-dipole interactions, dispersion interactions and hydrogen bonding.

Chemical adsorption, (chemisorption) is also based on electrostatic forces, but much stronger interactive forces play a greater role on this process (Sawyer *et al.*, 1994). In chemisorption, the attraction between adsorbent and adsorbate is a covalent or electrostatic chemical bond between atoms, with shorter bond length and higher bond energy. Generally, the magnitude of adsorption enthalpy energy (ΔH) value lies in the range of 40–120 kJ mol^{-1} for chemisorption mechanisms (Alkan *et al.*, 2004).

2.5.1 Adsorption Equilibrium Isotherms

An adsorption isotherm is a mathematical model that describes the distribution of the adsorbate between liquid and solid phases, based on a set of thermodynamic assumptions related to the heterogeneity/homogeneity of the solid surface, the type of coverage, and the likelihood of interaction between the adsorbate species. The equation parameters of these equilibrium models provide insight into both the sorption mechanism and the surface properties and affinity of the sorbent. Among the widely used adsorption isotherms, only a few used for describing adsorption on mesoporous materials (Jovan *et al.*, 2006), will be discussed here.

2.5.1.1 Freundlich Isotherm:

A brief empirical equation often used to represent adsorption data is called the Freundlich equation (Freundlich, 1906). The Freundlich isotherm describes non-ideal sorption on heterogeneous surfaces as well as multilayer sorption. The empirically derived Freundlich isotherm is defined as shown below;

$$q_e = K_f C_e^{1/n} \qquad \text{Equation 1}$$

Where; q_e : Amount adsorbed per unit weight of adsorbent at equilibrium (μg g^{-1})
C_e : Equilibrium concentration of adsorbate in solution after adsorption (μg g^{-1})
K_f : Empirical Freundlich constant or capacity factor (μg g^{-1})
$1/n$: Freundlich exponent

The Freundlich exponent $1/n$ is descriptive of the diversity of free energies associated with the adsorption of the solute by multiple components of a heterogeneous adsorbent. When $1/n = 1$, the isotherm is linear and the system has a constant free energy at all adsorbate concentrations. When $1/n < 1$, the isotherm is concave and adsorbates are bound with weaker and weaker free energies, and when $1/n > 1$, the isotherm is convex and more adsorbate presence in the adsorbent enhance the free energies of further adsorption (Schwarzenbach, 2003).

The good fit of Freundlich isotherm to an adsorption system implies there is almost no limit to the amount of substance adsorbed and there is a multilayer adsorption. The applicability of the Freundlich equation to a given system is tested by plotting log q_e against log C_e from the logarithmic form of Equation 2.0.

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad \text{Equation 2}$$

Such a plot should yield a straight line with intercept equal to log K_f and slope equal to *1/n.* Freundlich isotherm is often criticized for lacking a fundamental thermodynamic basis since it does not reduce to Henry's law at low concentrations.

2.5.1.2 Langmuir Isotherm:

An alternative equation was derived by Langmuir on the basis of a definite case of the nature of the process of adsorption from solution (Langmuir, 1916). The Langmuir adsorption isotherm was developed assuming that; a fixed number of accessible sites are available on the adsorbent surface, all of which have the same energy, adsorption is reversible, monolayer adsorption occurs and that there are no lateral interactions among the adsorbates.

It is one of the most widely used adsorption isotherms since it produces appreciable agreement with a wide variety of experimental data. The Langmuir adsorption isotherm is defined as:

$$q_e = \frac{K_L C_e Q_m}{1 + K_L C_e} \qquad \text{Equation 3}$$

Where; q_e : Amount adsorbed per unit weight of adsorbent at equilibrium (μg g^{-1})

C_e : Equilibrium concentration of adsorbate in solution after adsorption (μg L^{-1})

Q_m: Empirical Langmuir constant which represents maximum adsorption capacity (μg g^{-1})

K_L : Empirical Langmuir constant (L μg^{-1}) (Omri *et al.*, 2012).

The Q_m represents the total number of surface sites per unit weight of adsorbent. Ideally, Q_m would be equal for all adsorbates. However, Q_m vary between different compounds because of differences in adsorbate sizes. Therefore, it describes the maximum achievable surface concentration of a given compound. The constant K_L, the Langmuir constant, is defined as the equilibrium constant of the adsorption reaction. The K_L implies a constant adsorbate affinity for all surface sites (Schwarzenbach, 2003).

Rearranging the above equation (3) we obtain the equation below:

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \qquad \text{Equation 4}$$

and plotting of C_e/q_e against C_e gives a straight line with slope $1/Q_m$ and intercept $1/Q_m K_L$. At low sorbate concentrations the Langmuir isotherm effectively reduces a linear isotherm and thus follows Henry's law. Alternatively, at high sorbate concentrations, it predicts a constant – monolayer – sorption capacity.

2.5.1.3 Temkin Isotherm:

Temkin adsorption isotherm was developed assuming that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate–adsorbate interactions and that the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy (Aharoni and Ungarish, 1977)

The Temkin isotherm is represented by following equation (Aharoni and Sparks, 1991):

$$q_e = \frac{RT}{b}\log(K_T C_e) \qquad \text{Equation 5}$$

Equation 5 can be expressed in its linear form as:

$$q_e = B_T \log K_T + B_T \log C_e \qquad \text{Equation 6}$$

Where B_T : $\frac{RT}{b}$ (Temkin constant related to the heat of adsorption(kJ mol^{-1})

R : Gas constant (8.314 J mol^{-1} K^{-1})

T : Temperature (K)

K_T : Emprical Temkin constant related to the equilibrium binding constant related to the maximum binding energy (L µg^{-1}).

The adsorption data can be analyzed according to the Equation 6. A plot of the q_e versus log C_e enables the determination of the isotherm constants K_T and B_T (Sristeva *et al.*, 2006).

2.6 Adsorption thermodynamics

Temperature is an important factor in assessing thermodynamic feasibility of adsorption processes due to its influence on water solubility of pesticides, diffusion rate of molecules to the binding sites and chemical sorption reactions (Daneshvar *et al.*, 2007; Hameed, 2007). The thermal stability of pesticides is also an important parameter in thermodynamic studies. In the present study, the effect of temperature was studied at 293, 303 and 323 K within the range of most thermodynamic studies (Hameed, 2007; Ahmed and Theydan, 2012). Both tebuconazole and clomazone are known to be stable at room temperature (298 K), for at least two years and stable at 323 K for at least 3 months (Tomlin, 2003). The nature of the adsorption process is mostly defined by the calculated adsorption enthalpy energy (ΔH), Gibbs free energy (ΔG) and entropy (ΔS).

Negative enthalpy energy (ΔH) values indicate the adsorption process is exothermic and positive values imply the process is endothermic (Hameed, 2007). The magnitude of the enthalpy value is also indicative of the type of the adsorption process. Generally, the magnitude of the ΔH value ranging from 2.1- 20.9 kJ mol^{-1} corresponds to physical sorption (Saha *et al.*, 2010) and 40–120 kJ mol^{-1} for chemisorption mechanisms (Alkan *et al.*, 2004).

Gibbs free energy (ΔG) is a measure of the natural tendency, spontaneity, for a process to occur. Negative ΔG values imply that the adsorption reaction is thermodynamically spontaneous and is non-spontaneous for positive ΔG values (ElShafei *et al.*, 2009). An increase in negative values of Gibbs free energy, ΔG, with increase in temperature shows an increase in feasibility of adsorption of the pesticides at higher temperatures (Ahmed and Theydan, 2012).

Entropy (ΔS) is a measure of the degree of randomness at an interface by measurement of the energy dispersed in the process. Negative values of ΔS suggest a decrease in the randomness at sorbate–solution interface during the adsorption process (Ahmeda and Theydan, 2012). Positive ΔS is attributed to increasing disorder which may be related to the extent of hydration of the adsorbate molecules (ElShafei *et al.*, 2009). In this study, the adsorption behaviour of tebuconazole and clomazone by NaX is investigated. A systematic study on the adsorption kinetics onto NaX was conducted and effect of pesticide concentration, contact time/kinetics, thermodynamic parameters and the site of adsorption on the zeolite framework was studied.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Reagents and Instruments

Faujasite X (NaX) (Si/Al = 1.5), 0.2 μm particle size was obtained from Sigma-Aldrich Chemical company, (St Louis, MO, USA). The HPLC grade methanol and acetonitrile were supplied by Mallinckrodt- (NJ, USA), phosphoric acid (85%) was supplied by Merck- (Brazil), tebuconazole (purity 98%) and clomazone (purity 98%) standards were supplied by Dr. Ehrenstorfer-Laboratory (Germany).

For instrumentation, water purifier Milli-Q system UV3 Direct (18.2 MΩ cm resistivity) from Millipore (Bedford, MA, USA), analytical balance accurate model APX 200 (Denver Instrument, USA), Ultrasound bath Bandelin Sonorex RK 510 (Walldorf, Germany), Vacuum Pump Tecnal TE-058 (Piracicaba, SP, Brazil), Liquid Chromatograph Varian (Palo Alto, CA, USA), equipped with pump model 210, diode array detector (DAD) Pro Star 335, data acquisition system Star Workstation 6.0, analytical column Gemini 5 μ C_{18} (250 × 4.6 mm id; 5 μm) and guard column (20 × 1 mm) of the same material, both containing octadecylsilane-modified silica (Phenomenex, Torrance, CA, USA), X-ray diffractometer D8 Advance from Brucker (Germany) with copper radiation (K_α=1.5406), Perkin Elmer (400 FT-IR spectrometer) with ATR (attenuated total reflection) attached and automatic micropipettes with variable capacity (Brand, Germany and Eppendorf, Canada) were used.

3.2 Chromatographic procedures

Quantification was done using validated and used methods for tebuconazole and clomazone determination in water by High Pressure Liquid Chromatography with Diode Array Detection (HPLC-DAD). Tebuconazole and clomazone were detected at 220 nm and 212 nm respectively. The mobile phase for determination of tebuconazole was a mixture of acetonitrile and water (70:30 v/v) at pH 3 with an injection flow rate of 1 mL min^{-1} (Vicari, 2009). The mobile phase for clomazone determination was a mixture of acetonitrile and water (60:40 v/v) at pH 3 with a flow rate of 0.8 mL min^{-1} (Zanella *et al.*, 2002). The pH of the mobile phase was adjusted to pH 3 using phosphoric acid (1:1 v/v) (Zanella *et al.*, 2003). An injection volume of 20 μL was used. The calibration curve was constructed for each pesticide in the concentration range 100-1000 μg L^{-1} prepared in HPLC grade methanol for tebuconazole and in acetonitrile for clomazone. High concentration pesticide concentrations, 1024 mg L^{-1} tebuconazole and 1947 mg L^{-1} clomazone, were prepared in methanol and acetonitrile respectively, since the polar solvents provide complete solubilization of the analytes. The standard stock solutions were stored at 279 K and used to spike ultrapure water samples to the required concentrations.

3.3 Activation of the zeolite

The NaX was activated under 200 mmHg vacuum. A mass of 50 g of zeolite was weighed in a flask and then evacuated for 30 minutes. The contents were then heated at 343 K and continuous heating was done by raising the temperature by 30 K every 30 minutes up to 403 K. Finally, the temperature was raised to 423 K and heating was maintained for 105 minutes. The flask was allowed to cool at room temperature and the contents transferred to a sealed glass bottle for use (Ogunnah *et al*., 2013).

3.4 Adsorption Isotherm Experiment

3.4.1 Effect of pesticide concentration on adsorption extent

Adsorption of the pesticides was determined in a batch adsorption experiment. Here, 0.1 g of activated NaX was dispersed into Erlenmeyer flasks containing 50 mL of various concentrations of tebuconazole (100, 250, 500, 700 and 1000 μg L^{-1}) prepared by dilution of the stock solution. The flasks were magnetically stirred at 300 rpm at 303 K. The pH values of all the solutions were found to be in the range of 8.0-9.0 for all tests unless otherwise indicated. After pseudo-equilibration for 1 h, the solution was decanted and the supernatant filtered through 0.2 μm filters. Volumes of 1.0 mL aliquots were withdrawn and transferred into sealed glass vials for residual pesticide analysis. A control experiment was set-up to confirm whether any tebuconazole was adsorbed on the glass container. The concentration of the pesticide adsorbed on the zeolite was calculated as the difference between the spiked amount and the residual concentration after equilibration. Similar treatments were repeated for clomazone at 293 K adopting the method by El Bakouri *et al*. (2009).

3.4.2 Thermodynamic study

For the effect of temperature on adsorption study, the method by Moussavi *et al*. (2013) was adopted. Exactly 0.1 g of activated NaX was dispersed into 50 mL of 500 μg L^{-1} of tebuconazole and stirred at 300 rpm at 303 K. After equilibration for 1 h, 1.0 mL aliquots were withdrawn from the flask and transferred into sealed glass vials for residual pesticide analysis. Similar separate treatments were repeated at different temperatures (293 and 323 K). The experiments were repeated for clomazone at 293, 303 and 323 K within the temperature range of most thermodynamic studies (Hameed, 2007; Ahmed and Theydan, 2012; Alkan *et al.*, 2004; Saha *et al.*, 2010).

3.4.3 Effect of Contact time on adsorption extent (kinetics)

To study the effect of contact time, the adsorption kinetic experiments were performed by batch technique according to Organization for Economic Cooperation and Development guideline for testing of chemicals (OECD, 2000). A mass of 0.1 g of activated zeolite X was dispersed into 50 mL of 500 $\mu g\ L^{-1}$ of tebuconazole at 303 K and stirred at 300 rpm. At intervals (0, 0.5, 1.5, 2.5, 3.5, 5.5 and 6.5 h), 0.5 mL aliquots were withdrawn from the flasks and transferred into sealed glass vials for residual pesticide analysis, making a total of 6% of the total volume. The peak area at each interval was converted to concentration using the working calibration curve. Similar treatment was done for clomazone at 293 K and sampling done at predetermined time intervals. Measurements were carried in duplicate for all experiments. The used zeolites were then characterized using X-ray Diffraction (XRD) and Fourier Transform Infrared spectroscopy (FT-IR) techniques in order to elucidate the mechanism and site of adsorption of tebuconazole and clomazone onto NaX. The XRD instrument settings were 40 kV, 30 mA, step size of 0.02^{o} (2θ) and a scan rate of $2\theta\ \text{min}^{-1}$ for $5^{o} \leq (2\theta) \leq 45^{o}$ (Ogunnah *et al.*, 2013) while FT-IR spectra was obtained in the range 400-4000 cm^{-1} (Nezamzadeh and Salimini, 2010). The experimental kinetic data was used for determination of pseudo-equilibrium time used for effect of initial pesticide concentration experiments described in section 3.4.1.

3.5 Data analysis

The concentrations of each pesticide obtained from the experiments above were linearly regressed to establish the relationship between concentration, time and temperature. Statistical evaluation of differences among the experimental results was determined by Analysis of variance (ANOVA). Statistical significant difference $p<0.05$ between the pesticide adsorption and initial pesticide concentrations were performed to examine the significant differences among means using MSTATC program.

3.6 Determination of adsorption isotherm

The equilibrium concentrations were expressed in terms of distribution coefficient (K_d) and percent adsorption. Distribution coefficient (K_d) was obtained using the relation below;

$$K_d = \frac{Amount\ of\ pesticide\ in\ adsorbent}{Amount\ of\ pesticide\ in\ solution} \times \frac{V}{m} \qquad \text{Equation 7}$$

Where V is the volume of solution in L and m is the mass of adsorbent in g while the percent adsorption is given by:

$$\%pesticide\ adsorbed = \frac{C_\circ - C_e}{C_\circ} \times 100 \qquad \text{Equation 8}$$

Where C_o and C_e are the intial and equilibrium concentrations respectively

Adsorption isotherms of the pesticides on the NaX were constructed by fitting the concentrations adsorbed and concentrations in solution to linearized forms of well-known adsorption isotherm equations, namely Langmuir, Freundlich and Temkin models (Table 3). The best fit equation describing the experimental data was determined by the R^2 values of the regression lines. The equilibrium adsorption capacity, q_e, at different concentrations was obtained by the equation below:

$$q_e = \frac{V(C_\circ - C_e)}{mC_\circ} \qquad \text{Equation 9}$$

Table 3: Adsorption isotherm equations and parameters

Isotherm Model	Equation	Reference	Parameters
Langmuir	$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{Q_m K_L C_e}$	(Langmuir, 1918)	Q_m(μg/g) , K_L (L/g)
	$R_L = \frac{1}{1 + K_L C_\circ}$	(Hall et al., 1966)	R_L
Freundlich	$\log q_e = \log k_f + \frac{1}{n}\log C_e$	(Freundlich, 1906)	K_f, n
Temkin	$q_e = B\ln A_T + B\ln C_e$	(Temkin, 1940)	B, A_T

3.7 Determination of thermodynamic parameters

The effect of temperature was studied in the temperature range (293-323 K), to determine the thermodynamic feasibility of the adsorption process. The thermodynamic parameters (Table 4), namely, changes in Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were estimated using the following equations (Ahmaruzzaman *et al.*, 2010):

$$\Delta G^{\circ} = -RT\ln K_c \qquad \text{Equation 10}$$

$$K_c = \frac{C_{ad}}{C_e} \qquad \text{Equation 11}$$

Where K_c is the equilibrium constant, C_e is the equilibrium concentration in the solution (µg L^{-1}) and C_{ad} is the equilibrium solid phase concentration (µg L^{-1}). Enthalpy and entropy were obtained from slope and intercept of the Van't Hoff plot respectively (Ahmaruzzaman *et al.*, 2010).

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{2.303}\frac{1}{T} \qquad \text{Equation 12}$$

3.8 Determination of adsorption kinetics

The equilibrium sorption data was studied using two kinetic models, namely pseudo-first order and pseudo-second order models (Table 4) in order to predict the adsorption rate which controls the equilibrium time. This was because previous similar studies have indicated that pesticides adsorption on mesoporous materials mostly conform to 1st and 2nd pseudo-order kinetics (Yousef *et al.*, 2011). The amount of pesticide adsorbed at any time t, q_t (µg adsorbate/g adsorbent), was calculated using the following mass balance equation:

$$q_t = \frac{(C_0 - C_t)}{m}V \qquad \text{Equation 13}$$

Where C_o and C_t (µg L^{-1}) are the initial and liquid-phase concentrations of the adsorbate, respectively, at any time t, V is the pesticide solution volume (L), and m is the adsorbent mass (g).

Table 4: Kinetic models for removal of tebuconazole and clomazone by NaX

Kinetic model	**Equation**	**Reference**
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	(Ho, 2006)
Pseudo-first order	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$	(Ho, 2004)

3.9 Determination of adsorption mechanism

The sorption kinetic data were fitted to intraparticle diffusion model (Weber *et al.*, 1963) in order to determine the rate controlling step in the adsorption process. The model is represented by the expression:

$$q_t = k_p t^{0.5} + C \qquad \text{Equation 14}$$

Where q_t is the amount of tebuconazole adsorbed at equilibrium (µg g^{-1}) at time t, k_p is the intraparticle diffusion rate constant (g µg^{-1}h^{-1}) and C is the intercept. From the model, if the regression of q_t as a function of $t^{0.5}$ is linear then intraparticle diffusion occurs and if the line passes through the origin, then intraparticle diffusion is the only rate-limiting step. Otherwise, a different mechanism along with intraparticle diffusion occurs (Yousef *et al.*, 2011).

CHAPTER FOUR

RESULTS

4.1 Calibration Curves for residual tebuconazole and clomazone quantification

The calibration curves for quantification of residual pesticides concentrations afforded a linear regression coefficient, $R^2 > 0.99$ for each pesticide. The equations are listed in Table 5. The control analysis indicated that undetectable amounts of the pesticide were adsorbed on the glass container walls while the pH changes following the treatment with zeolite were in the range 8-9 for all samples and hence were considered of negligible effect as a variable in the adsorption process. Also, degradation product was detected for both pesticides.

Table 5: calibration equations and the correlation (R^2) for quantification of pesticides under study

Compound	Equation	R^2
Tebuconazole	$y = 653.5x + 305.8$	0.999
Clomazone	$y = 1286.x + 15036$	0.997

4.2 Effect of initial pesticide concentration on adsorption extent

A constant mass of NaX (0.1 g) was dispersed into various concentrations of each pesticide to evaluate the effect of initial pesticide concentration on the extent of adsorption. When NaX was dispersed into various pesticide concentrations (100-1000 $\mu g\ L^{-1}$); the adsorption extent varied significantly ($p<0.05$) with the initial concentration of the pesticide, for both tebuconazole and clomazone. The confidence level data are listed in Table 6. NaX showed a greater adsorption of tebuconazole at lower initial concentrations while clomazone was least adsorbed at low initial concentration (Fig. 4).

Table 6: Confidence level for effect of concentration

pesticide	Percent confidence level (95.0%)
Tebuconazole	0.0060
Clomazone	0.0006

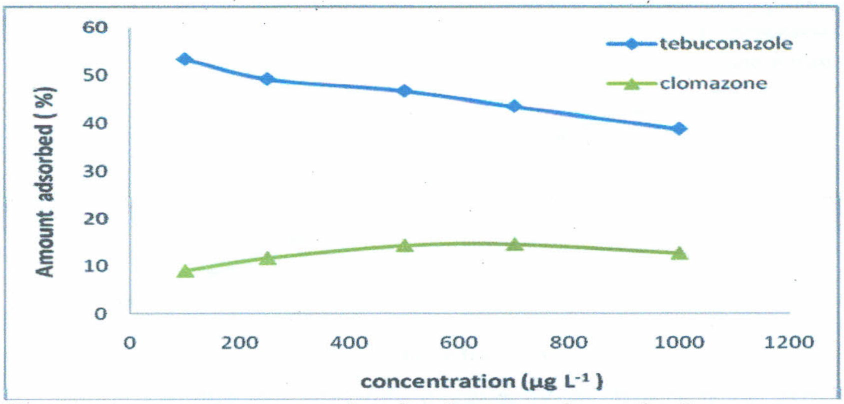

Figure 4. percent removal of tebuconazole and clomazone as function of initial concentration: Adsorbent=0.1 g /50 mL, time=60 min

4.2.1 Tebuconazole

The amount of each pesticide adsorbed at each concentration was expressed as percent (%) for a constant mass of adsorbent. The percentage tebuconazole adsorption decreased with increase in concentration, Fig. 4, from 53 to 39%, when the initial concentration was increased from 100 to 1000 µg L^{-1} for adsorbent dosage of 0.1 g/50 mL at 303 K. The distribution coefficient (K_d) also decreased with increase in tebuconazole concentration (Fig. 5). However, the equilibrium adsorption capacity increased almost linearly up to 500 µg L^{-1} initial pesticide concentration (Fig. 6).

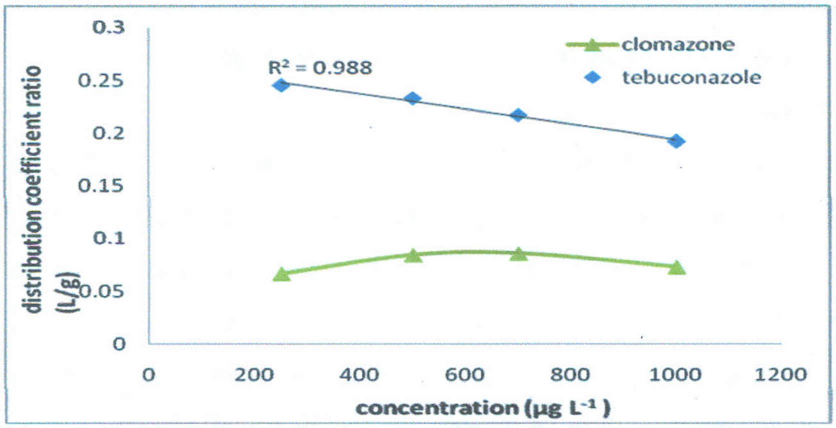

Figure 5. Variation of tebuconazole and clomazone distribution coefficient (K_d) as function of their initial concentration: Adsorbent=0.1 g/50 mL, time=60 min

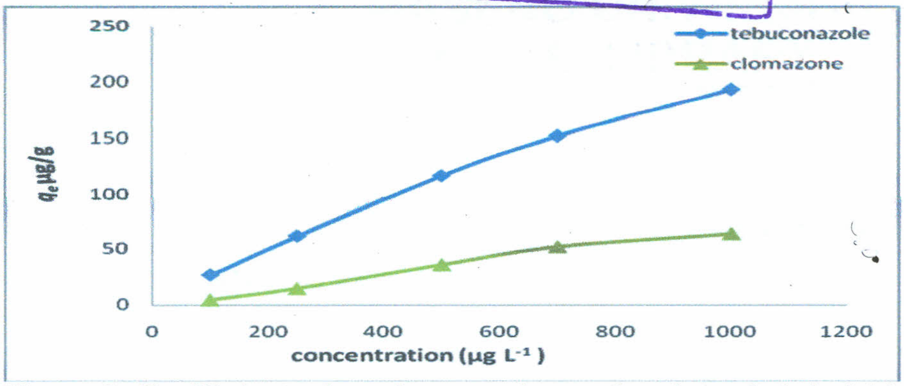

Figure 6. Equilibrium adsorption capacity as function of their initial concentration: Adsorbent=0.1 g/50 mL, time=60 min

4.2.2 Clomazone

As opposed to the trend for tebuconazole, the equilibrium adsorption, Fig. 4, showed that the amount of clomazone adsorbed increased with an increase in initial pesticide concentration. Beyond 500 µg L^{-1} a near plateau was observed i.e. there was little variation in percentage adsorption. When the initial concentration is increased from 100 to 1000 µg L^{-1}, the adsorption capacity at equilibrium increased from 4 to 63 µg g^{-1} (Fig. 6) for adsorbent dosage of 0.1 g/50 mL at 293 K. However, the distribution coefficient (K_d) decreased at concentration above 700 µg L^{-1}.

4.3 Isothermal studies for tebuconazole and clomazone onto NaX

The adsorption capacity of NaX for the two pesticides was investigated by fitting the equilibrium data to three well-known adsorption isotherms, namely, Langmuir, Freundlich and Temkin isotherms (Table 3) and the goodness of fit tested using the R^2 values. The experimental sorption data corresponded to the adsorption isotherm models in the order Langmuir>Freundlich> Temkin for both pesticides studied. The plotting of linearised Langmuir model resulted in $R^2 = 0.999$, indicating that the Langmuir isotherm model best described the adsorption pattern of tebuconazole and clomazone on NaX, with correlation coefficient R^2 value, closest to unity. However, a negative intercept was obtained for the Langmuir isotherm model for clomazone, yielding negative constants. The calculated isotherm parameters and regression coefficients are listed in Table 7.

Table 7: Calculated isotherm parameters

pesticide	Isotherm model	Calculated isotherm constants
Tebuconazole (303K)	**Langmuir**	Q_m(μg/g) = 500
		K_L (L/g) = 0.0012
		R_L = 0.4545
		R^2 = 0.999
	Freundlich	K_f, = 1.3459
		n = 1.2739
		R^2 = 0.994
	Temkin	B = 64.88
		A_T = 0.026
		R^2 = 0.96
Clomazone (293K)	**Langmuir**	Q_m(μg/g) = -58.82
		K_L (L/g) = -8.04×10^{-4}
		R^2 = 0.999
	Freundlich	K_f, = 4.168×10^{-3}
		n = 0.6901
		R^2 = 0.977
	Temkin	B = 66.14
		A_T = 0.132
		R^2 = 0.946

The adsorption isotherms are shown in appendices 3-8.

4.4 Thermodynamics of tebuconazole and clomazone adsorption onto NaX

The thermodynamic parameters were studied at temperatures 293, 303 and 323 K to determine the thermodynamic feasibility of the adsorption process for each pesticide at 500 μg L^{-1} pesticide concentration. The thermodynamic parameters for adsorption of each pesticide on NaX, namely changes in, Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were estimated using Van't Hoff plot (Fig. 7) and the calculated values are listed in Table 8.

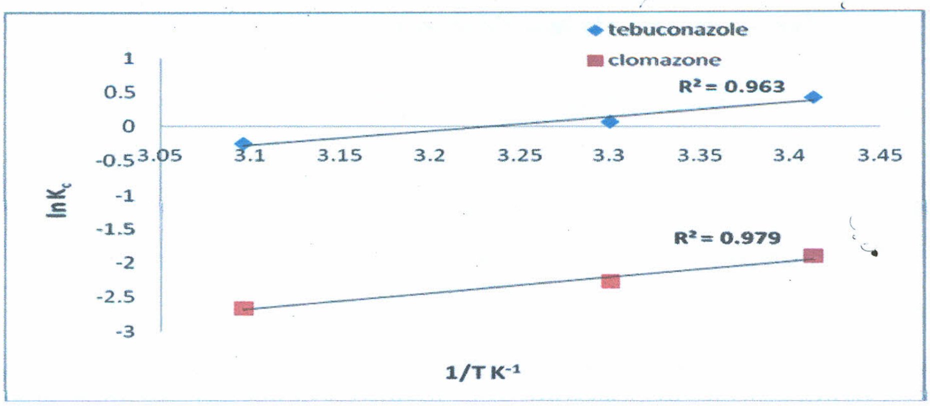

Figure 7: Van't Hoff plot for adsorption of tebuconazole and clomazone on NaX (Concentration 500 µg L^{-1}, Adsorbent=0.1 g/50 mL, time=60min).

Table 8: Calculated thermodynamic parameters and variation of percent pesticide adsorbed by NaX at different temperatures

Pesticide	**Temp (K)**	**Amount Adsorbed %**	ΔG **(Jmol^{-1})**	ΔH **(kJmol^{-1})**	ΔS **(Jmol^{-1}K^{-1})**
Tebuconazole	293	60.3	-1059.0	-38.7	-54.4
	303	51.8	-180.7		
	323	43.9	613.1		
Clomazone	293	12.9	4635.9	-44.9	-82.7
	303	9.4	5719.6		
	323	6.5	7155.4		

As the temperature varied from 293 to 323 K the percent removal of tebuconazole decreased from 60 to 43%. However, when the temperature was increased to 323 K, a positive ΔG value was recorded.

Positive ΔG values were obtained at all the temperatures tested for clomazone adsorption onto NaX with a negative ΔH value as well. When the temperature was raised from 293 to 323 K, the amount of clomazone adsorbed decreased by half. No degradation products were detected for all experiments and chromatograms depicted single peaks corresponding to the pesticide under study.

4.5 Adsorption kinetics of tebuconazole and clomazone on NaX

The equilibrium sorption data for tebuconazole and clomazone were fitted to both pseudo-first order and pseudo-second order adsorption kinetic models in order to predict the adsorption rates. The low R^2 value for pseudo-first order model revealed a very poor fitting of this model with the experimental data for both pesticides. The pseudo-second order model (Fig. 8) accorded R^2 value of 0.97 and 0.99, for clomazone and tebuconazole respectively, well describing the sorption data. The initial sorption rate (S_{rate}) and adsorption half-life ($t_{0.5}$) was calculated using the equations described by Ho and McKay (1998) below and the results are listed in Table 9.

$$S_{rate} = k_2 q_e^2 \qquad \text{Equation 15}$$

$$t_{\frac{1}{2}} = \frac{1}{k_2 q_e} \qquad \text{Equation 16}$$

Table 9: Adsorption rates of removal of tebuconazole and clomazone by NaX, where n.d= not determined

Pesticide	**Kinetic model**	**Initial sorption rate (µg g min^{-1})**	**Adsorption half-life (hours)**	**Calculated R^2**
Tebuconazole	Pseudo-1st order	n.d	n.d	= 0.01
	Pseudo-2nd order	**41**	**0.0634**	**= 0.998**
Clomazone	Pseudo-1st order	n.d	n.d	=0.34
	Pseudo-2nd order	8.33	0.1177	=0.97

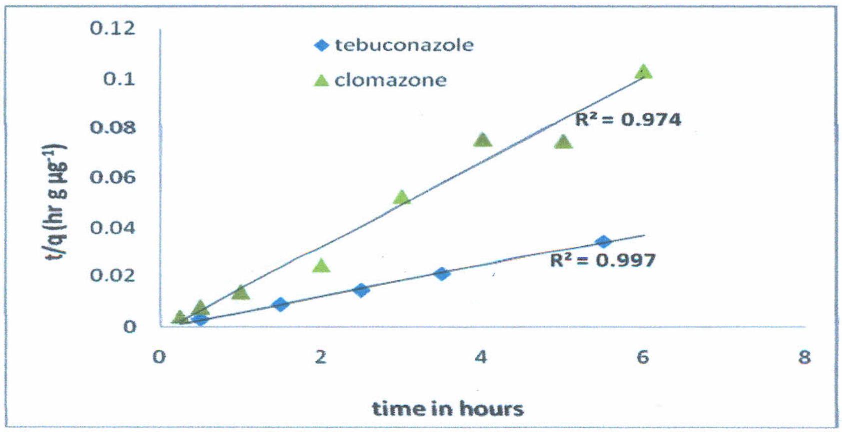

Figure 8. Pseudo-second order kinetics model for tebuconazole and clomazone (Concentration=500 µg L^{-1}, Adsorbent=0.1 g/50 mL)

For both pesticides studied, the amount of pesticide adsorbed increased for the first 1 h after which pseudo-equilibrium was assumed to have been reached since no further significant variation was observed. A sharp decrease in tebuconazole concentration was observed in the first 30 minutes (Fig. 9). Removal of at least 60% tebuconazole and 29% clomazone was recorded after 30 and 60 minutes of contact time, respectively.

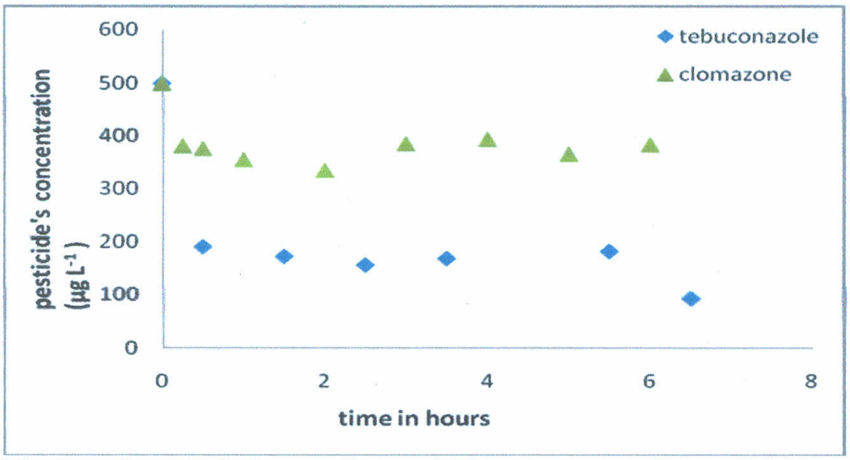

Figure 9. Variation of pesticide concentration with contact time (Initial concentration=500 µg L^{-1}, Adsorbent=0.1 g/50 mL)

The kinetic data for each pesticide was fitted to intraparticle diffusion model (Equation 8) to elucidate the adsorption mechanism and the rate limiting step of the adsorption process. The regression of q_t as a function of $t^{0.5}$ yielded multi-linear linear plot and did not pass through the origin for both pesticides (Fig. 10).

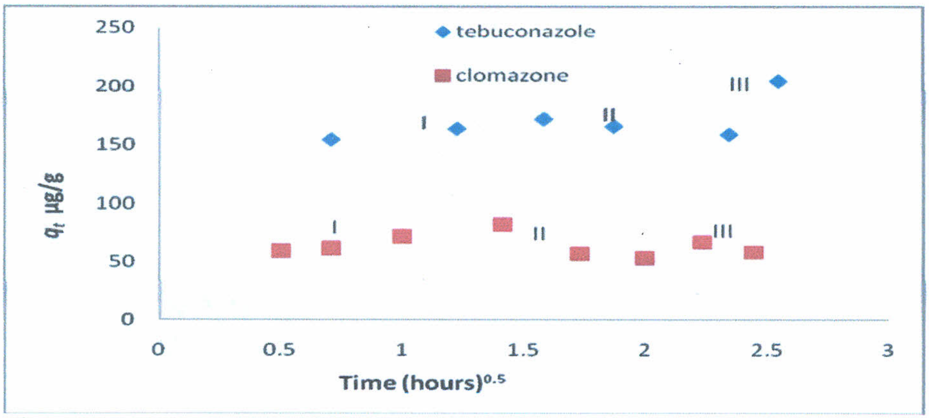

Figure 10. Intraparticle diffusion model for tebuconazole and clomazone adsorption ont NaX (Concentration= 500 µg L^{-1}, Adsorbent= 0.1 g/50 mL, I-III= phases of adsorption process)

4.6 Identification of pesticide site of adsorption on NaX

4.6.1 X-ray diffraction of NaX

After exposure of NaX to the pesticides, the diffractograms were right shifted by 0.5 (Fig. 11) and 0.6 (2θ) (Fig. 12) for tebuconazole and clomazone respectively for clarity. The exposure of faujasite X to tebuconazole resulted to a decrease in the relative intensities at both 9.9^0 (2θ) and 11.6^0(2θ) diffractograms (Fig. 11) while exposure of NaX to clomazone resulted to an increase in relative intensities (Fig. 12).

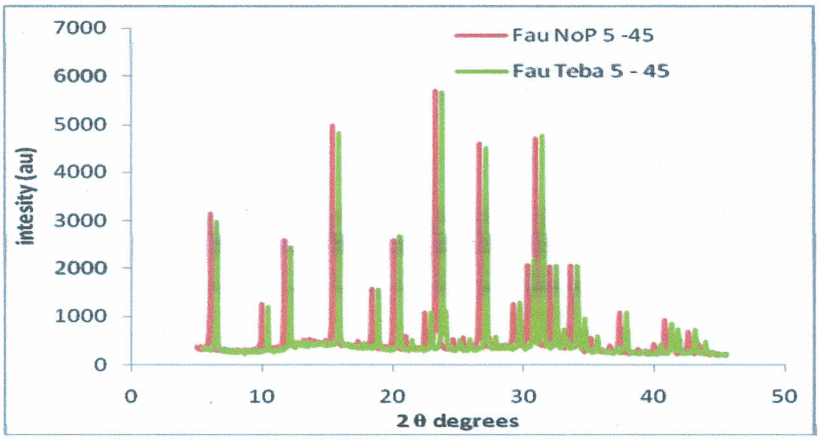

Figure 11. The XRD spectra for zeolite X in tebuconazole where Fau NoP= zeolite X with no tebuconazole, Fau teba= zeolite X with tebuconazole

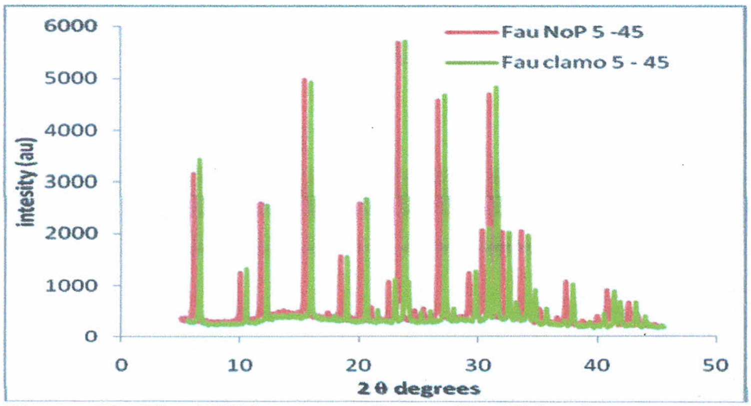

Figure 12. The XRD spectra for zeolite X in clomazone where Fau NoP= zeolite X with no tebuconazole, Fau clamo= zeolite X with clomazone

4.6.2 Infrared analysis of NaX

In the spectrum of free faujasite X samples, particularly worth considering were the band around 760±2 cm^{-1} resulting from the NaX single-four ring (S4R) vibrations. In this study, the NaX exposed to both tebuconazole and clomazone indicated a red shift of the

S4R from ca. 756 cm^{-1} to ca. 742 cm^{-1} (Table 10). Other than these vibrational bands, an additional weak band was observed at ca. 3365 cm^{-1}(Fig. 13). The complete finger-print is shown in appendices 9-11 and is summarized in Table 10 below.

Table 10: IR bands for NaX with tebuconazole and clomazone

Sample	**Observed band wave numbers cm^{-1}**			
NaX	679	756	1646	-
NaX+Tebuconazole	666	742	1638	3365
NaX+Clomazone	668	742	1629	3365

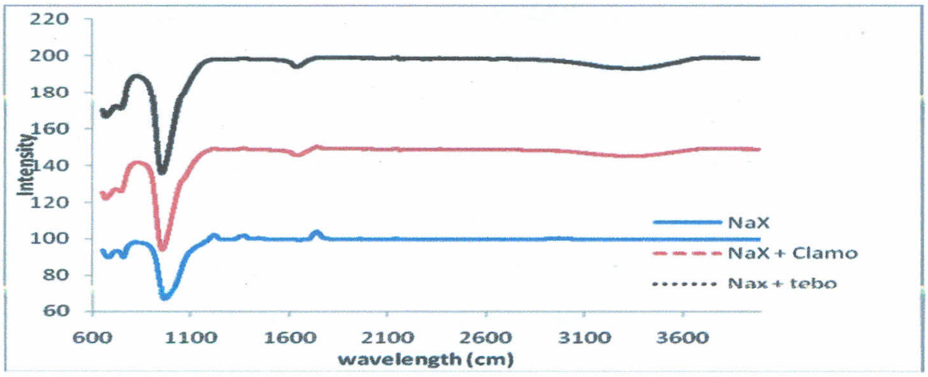

Figure 13. Infra-red spectrum of zeolite X in tebuconazole and clomazone where NaX is zeolite X without pesticide, Clamo is clomazone and tebo is tebuconazole.

CHAPTER FIVE

DISCUSSION

5.1 Effect of initial pesticide concentration on adsorption

For both tebuconazole and clomazone, the adsorption extent varied significantly ($p<0.05$) with the initial concentration of the pesticide (Table 6). This direct variation with concentration indicates that the initial pesticide concentration plays an important role in the adsorption of tebuconazole and clomazone on NaX and thus the suitability of NaX as an adsorbent depends on the initial concentration of the pesticide. The overall percent of initial tebuconazole adsorbed (equation 7) of the initial concentration decreased with increase in concentration from ca. 53 to ca. 39%, when the initial concentration is increased from 100 to 1000 μg L^{-1} for adsorbent dosage of 0.1 g/50 mL at 303 K (Fig. 4). This decrease in concentration is partly explained that at high initial concentration, tebuconazole molecules do not easily access the active adsorption sites probably due to steric hindrance and maximum sorption of the sorbate, hence the low percentage removal.

The progressive adsorption may be explained by the analysis of distribution coefficient (K_d) of the pesticide within the media (equation 8). The distribution coefficient was also observed to linearly ($R^2 = 0.986$) decrease with increase in tebuconazole concentration (Fig. 5), an indication that less energetically favored sites become involved in the adsorption process due to a limiting number of adsorption sites available for adsorption as adsorbate concentration increases. Jamil *et al.* (2011) had earlier reported similar observations for atrazine (dynamic diameter ca. 9.6 Å) removal using zeolite X prepared from Egyptian kaolin. The maximum adsorption capacity at equilibrium, q_e, for tebuconazole, increased linearly up to 500 μg L^{-1} above which further increase tended towards a plateau (Fig. 6). This also suggests that beyond 500 μg L^{-1} adsorption takes place on new less energetically favored surfaces, a scenario only possible in zeolites with involvement of its inner cavities.

On the contrast, at equilibrium, Fig. 4, the amount of clomazone adsorbed increased with an increase in initial pesticide concentration. Beyond 500 μg L^{-1} a near plateau was observed. When the initial concentration is increased from 100 to 1000 μg L^{-1}, the adsorption capacity at equilibrium increased from 4 to 63 μg $g^{-1}$for adsorbent dosage of 0.1 g/50 mL at 293 K (Fig. 6). High initial clomazone concentration led to an increase in the mass gradient between the solution and the adsorbent, thus mass transfer functioned as the driving force for the movement of the clomazone molecules from the bulk solution to the NaX surface. This observation is also in agreement with observations of Jalil *et al.* (2012) for malachite removal by bivalve shell-treated *zea mays* husk leaf and those of Ozcan *et al.* (2006) for adsorption of acid blue dye onto sepiolite.

Overall, at all concentrations tested, tebuconazole had higher distribution coefficient (K_d) values than clomazone (Fig. 5) indicating that tebuconazole is a strongly sorbing pesticide on NaX than clomazone, and is expected to exhibit a fast kinetic adsorbing process. This is typical behavior for pesticides with high sorption coefficients (El Bakouri *et al.*, 2009). This observation was attributed to the chemical structural differences and solubility of tebuconazole and clomazone as will be demonstrated later in section 5.6.

5.2 Adsorption isotherms of tebuconazole and clomazone onto NaX

Adsorption isotherms are mathematical models that are related with characteristic coefficients of the adsorption process which can be compared with coefficients obtained from various pesticide-adsorbent systems. In this study, adsorption data were fitted to Langmuir, Freundlich and Temkin models (Table 3) to determine which one is more applicable. The values of each model constants are listed in Table 7. Generally, the three models fit the experimental data with high correlation coefficients with Langmuir and Freudlich models giving coefficients closest to unity for both pesticides (Table 7).

The Langmuir monolayer maximum capacity parameter (Q_m=500 μg g^{-1}) for tebuconazole suggest that tebuconazole may have reached the saturation point of the active sites and any further adsorptions could only take place on new surfaces. According to Hall *et al.* (1966), the essential features of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (R_L). The value of R_L indicates the nature of the adsorption process to be either: unfavorable, $R_L>1$; linear $R_L=1$; favorable $R_L>0$; or irreversible $R_L=0$. Values of Freundlich constant $n>1$ represent favorable adsorption conditions as well (Ho and McKay, 1998). In the present investigation, both the Langmuir separation constant (R_L=0.4545) and Freundlich constant (n=1.2739) indicate that the sorption process of tebuconazole is favorable at 303 K. The value of 1/n is between 0 and 1 an indication that the surface of the adsorbent is heterogeneous. Such heterogeneity has been reported by Omri *et al*. (2012) on the adsorption study of bentazon on activated carbon. The depicted heterogeneity is consistent with the multi-active (I, II, & III) sites, channels and cages in NaX (Kowenje *et al*., 2006).

Similarly, the high R^2 values indicate that both Langmuir and Freundlich models describe the adsorption pattern of clomazone on NaX well. However, the negative values of the Langmuir isotherm constants (Q_m and K_L) indicate the inadequacy of the underlying assumptions of this model to explain clomazone adsorption process onto NaX, since these parameters represent non-negative characteristics of the sorbent and sorption process. Similar phenomenon was reported by Seki *et al.* (2006) for removal of boron by adsorption on Al_2O_3 based materials and by Maarof *et al*. (2004) for adsorption of phenol onto activated carbon. Thus, the Freundlich model was best fitted to describe the adsorption features of clomazone onto NaX.

As seen from the linear fit of Freundlich equation in Table 7, clomazone adsorption onto NaX was unfavorable as indicated by the Freundlich constant, *n*. This was attributed to the high water pesticide solubility and structural limitations of clomazone as discussed in section 5.6. This agrees with results reported by Seki *et al.* (2006) for boron adsorption onto Pural and Siral at 318 K. The Temkin isotherm model did not represent the data well relative to the other models for both pesticides.

5.3 Thermodynamics of adsorption of tebuconazole and clomazone onto NaX

The effect of temperature was studied at 293, 303 and 323 K to determine the thermodynamic feasibility of the adsorption process at 500 μg L^{-1} pesticide concentrations. This concentration was adopted as a model for real environmental samples since no published document so far obtained has reported tebuconazole and clomazone concentrations in water sources exceeding 500 μg L^{-1} (Elsaesser and Schulz, 2008; Mattice *et al*., 2010). Similar approach for determination of thermodynamic feasibility of an adsorption process at individual concentration of contaminant has been documented (Moussavi *et al*., 2013; Rauf *et al*., 2012; Khan *et al*., 2010). Experimental results showed a slight decrease of tebuconazole removal efficiency with increase in temperature, compared to clomazone, indicating a weak dependence of tebuconazole adsorption process on temperature relative to clomazone. As the temperature varied from 293 to 323 K the percent removal of tebuconazole decreased from 60 to 43%, while the amount of clomazone adsorbed decreased by half also indicative of an exothermic process (Table 8). This is a general behavior of adsorption process. The decrease in adsorption is attributable to the weakening of adsorptive forces between the active sites of the NaX and adsorbate molecules and also between the adjacent adsorbed molecules (Hameed, 2007) as a result of increased agitation energy. The decrease in adsorption can also be explained on the basis of solubility. Increase in temperature possibly afforded the pesticides more solubility in water and lowered their affinity for the adsorbent surface. This is consistent with other past studies by Daneshvar *et al.* (2007) and El Bakouri *et al.* (2009a) on pesticide adsorption onto various materials. Highest adsorption for tebuconazole onto NaX was recorded at 293 K hence temperatures higher than 303 K are not recommended.

The thermodynamic parameters namely changes in Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were estimated and the results are listed in Table 9. The negative ΔG (at 293 and 303 K) and ΔH values confirmed that the adsorption process of tebuconazole on NaX is both spontaneous and exothermic in nature respectively. Similar results have been reported for adsorption of phenol on synthetic NaY zeolite by Okolo *et al.* (2000). When the temperature was increased to 323 K, the reaction transitioned to non-spontaneity depicting the spontaneity of tebuconazole adsorption reaction is temperature dependent and more spontaneous at low temperature. Such phenomenon has also been reported for pesticides adsorption on various adsorbents (Alkan *et al.*, 2004).

Positive ΔG values obtained at all the temperatures tested and the negative ΔH for clomazone, indicates that clomazone adsorption onto NaX is non-spontaneous though exothermic under these experimental conditions. For both pesticides, the value of Gibbs free energy, ΔG, increased with increase in temperature suggesting that the exothermic nature of the reactions exceed the effect of increasing the diffusion rate as the temperature is raised. This is in agreement with results obtained by Al-Qodah *et al.* (2007) for adsorption of pesticides using oil shale ash. The increase in ΔG with rise in temperature indicates that the reaction becomes less feasible with increased temperature.

Generally, the magnitude of the ΔH value lies in the range of 40–120 kJ mol^{-1} for chemisorption mechanisms (Alkan *et al.*, 2004). In the present study, the ΔH values (38 kJ mol^{-1} and 44.9 kJ mol^{-1} for tebuconazole and clomazone, respectively) suggest a probable chemisorption mechanism for adsorption onto NaX. The negative values of ΔS obtained for both pesticides adsorption on faujasite X shows less randomness at the solid/solution interfaces during the adsorption process. This observation is consistent with molecules coming together or being anchored on a surface due to binding of sorbent molecules onto the NaX surface. Though the reliability of any data increases with increase in the number of data points, literature review presents numerous studies for which only three points of temperature, as in this study (Fig. 7), was sufficient to draw the relation using Van't Hoff equation (Muthanna and Samar, 2012; Ahmaruzzaman *et al.*, 2010; Damjanovic *et al.*, 2010; ElShafei *et al.*, 2009; Hameed, 2007). This restriction to closer temperature range is to avoid any possibility of structural changes to the reacting molecules. Both tebuconazole and clomazone are known to be stable at room temperature for at least two years and stable at 323 K for at least 3 months (Tomlin, 2003). No degradation products were detected in the present study, thus changes in pesticide concentrations were attributed to adsorption process. Further, 293 and 303 K are within ambient conditions applied in wastewater treatment. However, possible degradation may not be ruled out.

5.4 Effect of contact time/kinetics of tebuconazole and clomazone adsorption on NaX

The initial concentration of both pesticides was 500 µg L^{-1} for easy comparison of the adsorption behavior with contact time. The basis for this concentration is as previously explained. For both pesticides studied, the amount of pesticide adsorbed increased for the first 1 h after which pseudo-equilibrium was considered to have been reached since no further significant decrease was observed. Sorption studies indicate considerable variation in the time required to establish pseudo and dynamic equilibriums (de Wilde *et al.*, 2008). When equilibrium is attained, the adsorbate molecules in the bulk solution are in a state of dynamic equilibrium with the molecules adsorbed by NaX. In this study, pseudo-equilibrium was reached within 60 minutes. After pseudo-equilibrium, less than 4% variation of pesticide concentration in the solution was observed. Hence, in order to achieve a compromise between removal efficiency and the duration for complete analysis, 1 h was chosen as the pseudo-equilibration time for obtaining the adsorption isotherms. This conforms to previous results by Yonli *et al.* (2012) for removal of α-endosulfan from water by synthetic HY zeolites where equilibrium was established in less than 1 h. Pseudo-equilibrium, as in this study, has been widely applied and accepted in comparative isothermal studies of pesticides onto various sorbents (El Bakouri *et al.*, 2009; Kyriakopoulos *et al.*, 2005; Kumar and Philip, 2006). The sharp decrease in concentration observed in the first 30 minutes for both pesticides (Fig. 9) could be attributed to the large number of active adsorbent sites available at the beginning. After ca. 60 minutes, the adsorption extent is decreased. This phenomenon may be due to the difficulty of tebuconazole and clomazone molecules to access the less accessible inner active zeolitic sites, probably because of repulsion between the adsorbed molecules, those in bulk solution a characteristic of pseudo-equilibrium conditions (El Bakouri *et al.*, 2009).

The sorption data was studied using two kinetic models, namely pseudo-first order and pseudo-second order models in order to predict the adsorption rate which controls the equilibrium time. Previous similar studies have indicated that pesticides adsorption on mesoporous materials mostly conform to 1^{st} and 2^{nd} pseudo-order kinetics (Yousef *et al.*, 2011). The low R^2 value for pseudo-first order model (Table 9) reveals a very poor fitting of this model with the experimental data. Thus, the adsorption of tebuconazole and clomazone onto NaX is not a pseudo-first order reaction. However, the high correlation coefficients (R^2), 0.997 and 0.974 for tebuconazole and clomazone respectively, indicates that the experimental data is best described by the pseudo-second order model which is also consistent with a chemisorption mechanism (Omri *et al.*, 2012). The initial sorption rate (Table 9) for tebuconazole was almost five times greater than that for clomazone while the adsorption half-life of clomazone was twice that of tebuconazole. This relation was expected and is consistent with and corroborated by the distribution coefficient values reported earlier. Generally, pesticides with high sorption coefficient (K_d) values exhibit fast adsorption process. Similar trend was observed by El Bakouri *et al.* (2009a) in a comparative study on adsorption rates of aldrin, dieldrin and endrin pesticides onto acid-treated olive stones.

5.5 Mechanism of adsorption of tebuconazole and clomazone onto NaX

The sorption kinetic data were fitted to intraparticle diffusion model (Equation 8) in order to elucidate the adsorption mechanism and the rate controlling step in the adsorption process (Weber and Morris, 1963). From the model, when the regression of q_t as a function of $t^{0.5}$ (Fig. 10) is linear then intraparticle diffusion occurs and when the line passes through the origin, then intraparticle diffusion is the only rate-limiting step. Otherwise, a different mechanism concomitantly occurs with intraparticle diffusion (Yousef *et al.*, 2011).

Figure 10 indicates that both pesticides were adsorbed in a three-phased process, labeled I-III. The first linear phase (I) represents initial rapid adsorption which is characteristic of surface adsorption or boundary layer adsorption (El Bakouri *et al.*, 2009b). During the second phase (II) a decrease in adsorption was observed. This second phase could be attributed to the heterogeneity of the NaX surface and the attempt of the pesticide molecules to reptate through the smaller pores. The final phase (III) was attributed to adsorption-desorption processes simultaneously taking place due to pseudo-equilibrium. Similar results have been observed for adsorption of various compounds (Ozcan *et al.*, 2006; El Bakouri *et al.*, 2009b). Notably, neither of the plots passed through the origin. This indicates that though pore diffusion/reptation may be involved in the adsorption process of tebuconazole and clomazone onto NaX, it was not the rate-controlling step.

5.6 Identification of site of adsorption

X-ray diffraction is a technique employed to obtain information about atomic structure of crystalline substances. X-ray diffraction occurs when X-rays are scattered by atoms arranged in orderly array in crystals or powders. The atoms act as scattering centers hence information about the internal symmetry and arrangement of atoms in crystals and powders can be gained from relative intensities of the diffractograms (Moore and Reynolds, 1997). In the current study, the XRD analysis was performed to monitor cationic migrations from the zeolite framework. Such migrations would indicate participation of the Na^+ ions in the adsorption or catalytic breakdown process making the cations to act as point charges that attract the chlorine atoms in both tebuconazole and clomazone molecules. This mechanism of adsorption was postulated by Jamil *et al.* (2011) for adsorption of atrazine onto NaX prepared from Egyptian kaolin. Cationic migrations in sodium-type faujasite X are characterized by intensity changes for 9.9^0 (2θ) and 11.6^0(2θ) diffractograms (Kowenje *et al.*, 2010). XRD analysis of NaX exposed to both tebuconazole and clomazone (Fig. 11 and 12) indicated significant decrease and increase on the relative intensities of the diffractograms at 9.9^0 (2θ) and 11.6^0(2θ), respectively. These changes indicate that the cations participate in the adsorption process and the postulate by Jamil *et al.* (2011) applies corroborating a probable chemisorption mechanism. This finding also conforms to the results published by Ogunnah *et al.* (2013) for removal of malathion from water by synthetic NaX where a cation mediated process was reported. Since the Na^+ cations are involved in the adsorption process for both pesticides, the chemical structure and properties of the pesticides therefore play an important role in the extent of the adsorption process. The difference in the extent of adsorption of tebuconazole and clomazone onto NaX could be attributed to two factors.

First, the positions of the chlorine atoms on the substituted benzene ring of the pesticides seem to play a significant role on the adsorption extent of each pesticide. NaX showed better removal capacity for tebuconazole than clomazone. This may be attributed to the *para* position of chlorine in tebuconazole hence easier accessibility to the positive charges on the NaX unlike in clomazone where the chlorine atom is in *ortho* position rendering steric hinderance to the adsorption site. This *ortho* position would favor increased repulsion between adsorbed molecules as well. Secondly, the adsorption capacity was found to be inversely proportional to the water pesticide solubility (tebuconazole: 36 mg L^{-1}, clomazone 1100 mg L^{-1}). High solubility reduces the affinity of clomazone for the adsorbent surface (Daneshvar *et al.*, 2007). This coincides with results reported by de Wilde *et al.* (2008) for adsorption of isoxaben, linuron and isoproturon onto substrates used in biopurification systems.

FT-IR analysis was done to elucidate the adsorption mechanism and also identify the site of adsorption of the pesticides on the zeolite framework. Infrared spectra originate from different modes of vibration of a molecule, the main participants in the vibration being two atoms held together by a chemical bond. The vibrations have characteristic frequencies which primarily depend on the masses of the two vibrating atoms and the force constant of the bond between them given by the simple harmonic oscillator equation below (Nakamoto, 2002).

$$\bar{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{\frac{1}{2}} \qquad \text{Equation 8}$$

Where $\bar{\nu}$ is the absorption band in wavenumber (cm^{-1}), c is the velocity of light in cm s^{-1}, k is the force constant (N m^{-1}) and μ is the reduced mass (Kg) per molecule. Hence in case of an adsorption process, the attachment increases the reduced mass resulting to a decrease in vibration frequency/red shift. An increase in vibration frequency/blue shift is observed in case of dissociation process (Kowenje *et al.*, 2010).

In the spectrum of free faujasite X samples, particularly worth considering were the band around 760±2 cm^{-1} resulting from the NaX single-four ring (S4R) vibrations (Kowenje *et al.*, 2010). In this study, the NaX exposed to both tebuconazole and clomazone indicated a red shift of the S4R from ca. 756 cm^{-1} to ca. 742 cm^{-1} (appendices 9-11) confirming that both pesticides were adsorbed at the single-four-rings of the NaX framework. Since there was no blue shift observed, this also confirmed that there was no loss of cations from the sites. This observation is contrary to results by Ogunnah *et al.* (2013) for adsorption of malathion onto synthetic NaY zeolite where cation loss was reported. This can be explained by the stabilizing factor of Na^+ present in the supercage site III in NaX zeolite (Kanyi *et al.*, 2006). These results coupled with the fact that pore diffusion was not a rate controlling step strongly suggest that tebuconazole and clomazone were not adsorbed in the internal surfaces of the NaX matrix. It is therefore possible that the concentrations of tebuconazole and clomazone (100-1000 μg L^{-1}) used in this study and thus the amount adsorbed achievable was too low to cover the external surface of NaX hence the adsorbates did not reptate into the internal cavities of the zeolite framework. Furthermore, since both tebuconazole and clomazone are adsorbed at the same site on NaX and only a limited number of molecules can be accommodated per unit area of the active site, the effect of the position of chlorine atom seem to be the driving force dominating the overall effect of the molecular sizes of the pesticides.

In summary, the change in adsorption enthalpy ΔH values, a pseudo-second order kinetic adsorption reaction, participation of the cations and possible hydrogen bonding, binding at the S4R zeolitic active site and the fact that pore diffusion is not the rate controlling step are evidences that makes it conceivable that adsorption of tebuconazole and clomazone onto NaX is an external surface chemisorption process with the adsorbates in neutral forms.

Finally, since the amount of pesticide adsorbed is generally expected to increase with increase in NaX dosage due to increase in surface area and number of adsorption sites as noted by Garg *et al.* (2004), determination of the adsorbent dosage required for a given concentration of tebuconazole and clomazone is an important parameter for application in effluent treatment. Following that the adsorption studies indicate that Langmuir isotherm equation is adequately applicable to describe the adsorption data for tebuconazole; using Langmuir equation (Table 3) and equations 2 and 3, the amount of NaX required for a given volume of effluent can theoretically be estimated using the equation below (Omri *et al.*, 2012).

$$m = \frac{VRC_0\left[1 + K_L\left(C_0\left(1 - {R}/{100}\right)\right)\right]}{100Q_mK_L\left[C_0\left(1 - {R}/{100}\right)\right]} \qquad \text{Equation 10}$$

Where m is the mass of NaX (g) required to achieve a given removal efficiency (R) from wastewater of volume V (mL) for any given concentration of tebuconazole (μg L^{-1}) except for 100% removal conditions.

CHAPTER SIX

CONCLUSION AND RECOMENDATIONS

6.1 Conclusion

1. Initial pesticide concentration is a significant factor in assessing the suitability of NaX as an adsorbent for tebuconazole and clomazone removal from water.

2. Langmuir and Freundlich models gave the best fit for the experimental data for both pesticides. The maximum adsorption capacity for tebuconazole onto NaX, calculated from Langmuir isotherm, was 500 $\mu g\ g^{-1}$. Freundlich constant, *n,* obtained was 1.2739 and 0.6901 indicating that adsorption process was favorable and unfavorable for tebuconazole and clomazone, respectively.

3. The adsorption efficiency was found to decrease with increase in temperature. The calculated thermodynamic parameters, $-\Delta G$ (180.7 $J\ mol^{-1}$ at 303 K), $-\Delta H$ (38.7 $kJ\ mol^{-1}$) and $-\Delta S$ (54.4 $J\ mol^{-1}\ K^{-1}$) indicate that tebuconazole adsorption on NaX is spontaneous, exothermic and feasible while clomazone adsorption was non-spontaneous ($+\Delta G=5719.6\ J\ mol^{-1}$ at 303 K), exothermic ($-\Delta H=44.9\ kJ\ mol^{-1}$ and $-\Delta S=82.7\ J\ mol^{-1}\ K^{-1}$) and not feasible under the examined conditions.

4. The adsorption kinetics data were found to follow a pseudo-second order for both tebuconazole and clomazone. The half life was evaluated and the adsorption rate of tebuconazole (0.0634 h) was faster than that of clomazone (0.1177 h).

5. Intraparticle diffusion model showed that the adsorption of tebuconazole and clomazone onto NaX was multi-mechanistic (surface adsorption and possible reptation) and was not controlled by pore diffusion.

6. The adsorption of tebuconazole and clomazone onto NaX appears to be an external surface chemisorption adsorption process as indicated by FT-IR and XRD analysis. The pesticides are anchored at S4R zeolitic site and coulombic attraction of Na^+ and chlorine atoms is proposed as possible interaction mechanism.

7. NaX was found to be a better adsorbent for tebuconazole removal than clomazone at all concentrations tested.

6.2 Recommendations

Faujasite X (NaX) portrays suitability for wastewater treatment for agricultural wastewaters containing tebuconazole and probably other triazole fungicides and may be considered as an adsorbent subject to further feasibility studies. In such a case, NaX is recommended for application for low tebuconazole concentrations and temperatures above 303 K are not recommended.

6.3 Suggestion for further research

Studies should be conducted to determine:

1. The efficacy of NaX in removing other classes of pesticides from water at near real environmental concentrations
2. The efficacy of other zeolites in adsorbing other pesticides at near real environmental concentrations
3. Other suitable adsorbents for clomazone removal from water
4. The tunability of NaX for clomazone removal from water

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