INVESTIGATION OF ADSORPTION OF PESTICIDES BY ORGANO-ZEOLITE FROM WASTEWATER

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ABSTRACT

INVESTIGATION OF ADSORPTION OF PESTICIDES BY ORGANO-ZEOLITE FROM WASTEWATER

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The aim of this study was to determine the adsorption capacity of activated carbon and organo-zeolites for removal of pesticides in water.

In order to prepare organo-zeolite, two kinds of cationic surfactants, namely, hexadecyltrimethyl ammonium bromide (HTAB) and dodecyltrimethyl ammonium bromide (DTAB) were used. Adsorption studies of cationic surfactant on zeolite were investigated in respect to initial concentration of cationic surfactant, time, and temperature. It has been found that the best fitted isotherm equation was Langmuir equation. The observed adsorption rates were found to be equal to the second order kinetic model. The activation energies of cationic surfactant adsorption was determined by using Arrhenius equation. ΔS and ΔH values were also calculated from the van’t Hoff equation.

Adsorption of pesticides (2,4-D, propanil, diazinon, fenitrothion, trifluralin) onto activated carbon and organo-zeolite were investigated by evaluating the adsorption isotherms and fitting the data to Langmuir and Freundlich equations. The effects of initial concentration of pesticide, time, pH, and temperature on adsorption were investigated. Adsorption rates were calculated for each of pesticide. The activation energies of pesticide adsorption were determined by using Arrhenius equation. ΔS and ΔH values were also calculated from the van't Hoff equation.

Keywords: Adsorption, Zeolite, Cationic Surfactant, Pesticide, Adsorption Isotherm, Adsorption Kinetic, Adsorption thermodynamics.

ÖZ

ORGANO-ZEOLİT İLE ATIKSULARDAN PESTİSİT ADSORBSİYONUNUN İNCELENMESİ

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Bu çalışmanın amacı, sudaki pestisitlerin uzaklaştırılması için kullanılan organo-zeolitlerin ve aktif karbon adsorpsiyon kapasitelerini belirlemektir.

Organo-zeolit hazırlamak için iki çeşit katyonik yüzey aktif maddesi, hekzadesiltrimetil amonyum bromür (HTAB) ve dodesiltrimetil amoyum bromür (DTAB) kullanılmıştır. Zeolit üzerine katyonik yüzey aktif maddesi adsorbsiyonu çalışmaları başlangıç yüzey aktif maddesi konsantrasyonu, zaman ve sıcaklık bakımından incelenmiştir. Langmuir izotermi en uygun izotherm olarak bulunmuştur. Gözlenen adsorbsiyon oranları ikinci dereceden kinetik modele uymaktadır. Katyonik yüzey aktif maddesi adsorbsiyonu aktivasyon enerjileri için Arrhenius eşitliği kullanılmıştır. ΔS ve ΔH değerleri van't Hoff eşitliği kullanılarak hesaplanmıştır.

Aktif karbon ve organo-zeolit üzerine pestisitlerin (2,4-D, propanil, diazinon, fenitrothion, trifluralin) adsorbsiyonu, adsorbsiyon izotermleri değerlendirilerek ve verilere Langmuir ve Freundlich denklemleri uygulanarak araştırılmıştır. Başlangıç pestisit konsantrasyonu, zaman, pH ve sıcaklığın adsorpsiyona etkileri incelenmiştir. Adsorbsiyon hızları herbir pestisit için hesaplanmıştır. Pestisit adsorbsiyonu aktivasyon enerjisini bulmak amacıyla Arrhenius eşitliği kullanılmıştır. ∆S ve ∆H değerleri van't Hoff eşitliği kullanılarak hesaplanmıştır.

Anahtar Kelimeler: Adsorbsiyon, Zeolit, Katyonik Yüzey Aktif Maddesi, Pestisit, Adsorbsiyon Izotermi, Adsorbsiyon Kinetiği, Adsorbsiyon Termodinamiği.

To My Parents

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INTRODUCTION

71% of the planet's surface is covered by water. This essential substance is necessary for the continuation of life on Earth. Everyone needs clean water to meet regular needs. Clean water is used in most of activities of human beings such as agriculture, manufacture, transport, the industry (Inglezakis and Poulopoulos, 2006).

Most of the planet is covered by water; but only small amount of this water can be used as clean water. Approximately 97% of the earth's water is in the oceans, which is unhealthy for human consumption. 2% of the remaining 3% water is locked in the polar ice-caps. Less than 1% of the Earth's water is available as clean water in rivers, lakes, streams, reservoirs and ground water which are suitable for human consumption (De, 2003).

Freshwater is cleaned and transferred through the hydrological cycle in nature. Jana et.al. (2010) explained that "this natural process begins with the evaporation of water from the surface of the ocean. When moist air is lifted, it cools and water vapor condenses to form clouds. Moisture is transported around the globe until it returns to the surface as precipitation. Once the water reaches the ground, one of two processes may occur; some of water may evaporate back to the atmosphere or the water may penetrate the surface and become groundwater. Groundwater either seeps its way in the oceans, rivers, and streams, or is released back to the atmosphere through transpiration. The balance of water that remains on the Earth's surface is runoff which empties into lakes, rivers and streams and is carried back to the oceans, where the cycle begins again" (Jana et. al., 2010).

Nowadays, this process is insufficient as a result of human activities, discharge of various pollutants into the aquatic environment and specifically because of the thoughtless wasting of water.

Water pollution is the addition of substances that directly or indirectly change the nature of water body. Polluted water includes liquid waste discharged by domestic residences, from industry processes, and agricultural processes. As a result municipal wastewater contains a broad spectrum of contaminants (Figure 1.1).

The sources of municipal wastewater can be classified as being a point source or non-point source pollution. Point sources of pollution include wastewater treatment facilities, factories, and other sources. According to Environmental Protection Agency (1994) “nonpoint source (NPS) pollution comes from many sources. NPS pollution is caused by rainfall or snowmelt moving over and through the ground. As the runoff moves, it picks up and carries away natural and human made pollutants, which deposit in lakes, rivers, sea, and drinking water sources. These pollutants may contain the followings:

- Excess fertilizers, herbicides, and insecticides from agricultural lands and residential areas;
- Oil, grease, and toxic chemicals from urban runoff and energy production;
- Sediment from improperly managed construction sites, crop and forest lands, and eroding stream banks;
- Salt from irrigation practices and acid drainage from abandoned mines;
- Bacteria and nutrients from livestock, pet wastes, and faulty septicsystems;
- Atmospheric deposition and hydromodification are also sources of nonpoint source pollution” (EPA, 1994).

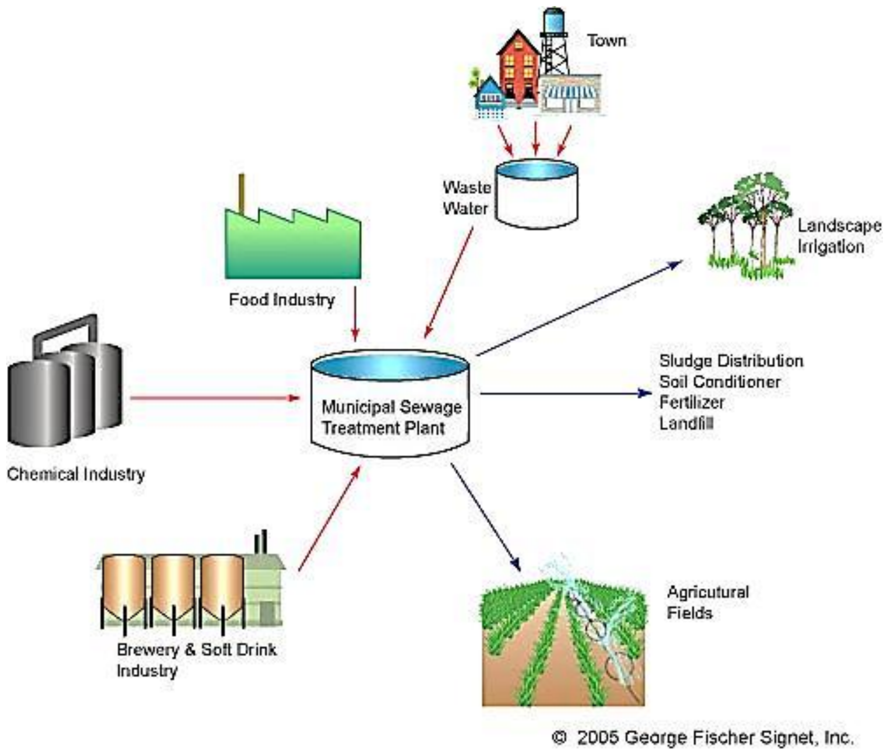


Figure 1.1 Sources of Municipal Wastewater

In addition, mineral treatment processes generally produced wastewaters containing varies pollutants. The pollutants in contaminated waters and/or wastewaters should be removed before using them again.

In the cleaning process varies methods and material can be used. These processes include chemical precipitation, biological processes for nitrification, phosphorus removal and physiochemical processes for filtration air stripping, oxidation, denitrification, ultrafiltration, reverse osmosis, ion exchange, electrodialysis, and adsorption on various adsorbents such as carbon and silicate and clay minerals.

Within this context various studies have been carried out previously. Some of them can be summarized as follow.

Two types of activated carbons was used to adsorb 2,4-dichlorophenoxyacetic acid in solutions of various pH. It was found that maximum adsorption occurred at at pH ≈ 2.5, which corresponds to the 2,4-D pK_a value (Belmouden et. al. 2000).

Aksu and Kabasakal (2004) studied on adsorption of 2,4-dichlorophenoxyacetic acid onto granular activated carbon as a function of initial concentration of adsorbate, pH, and temperature. Aksu and Kabasakal found that "in the adsorption mechanism of 2,4-dichlorophenoxyacetic acid, boundary layer and intraparticle diffusion played important roles for all temperature studied" .

Akçay et. al. (2005) studied the adsorption of 2,4-dichlorophenoxyacetic acid on organophilic sepiolite (dodecylammonium sepiolite) as a function of adsorbate concentration and temperature. They found that adsorption rates were equal to the first-order kinetics. Akçay et. al. (2005) claimed that, "the amount of adsorption of herbicide on organophilic sepiolite depends on the relative energies of adsorbent-adsorbate, adsorbate-solvent, and adsorbate-adsorbate interactions".

In another study, removal of herbicide 2,4-dichlorophenoxyacetic acid in aqueous solution by bituminous shale has been examined by means of batch technique (Ayar et. al., 2008). The results showed that, adsorption isotherm were fitted well with Freundlich, Dubinin-Radushkevic and Langmuir isotherm models. The adsorption capacities of the adsorbate were found to increase with increasing temperature and decreasing pH.

Adsorption of propanil from aqueous solution at activated carbon cloth was studied by Ayrancı and Hoda (2004b). They found that concentration of pesticide decreased in 2 hours. Equilibrium data were found to be fitted well with the Langmuir and Freundlich isotherm models.

Gonzalez et. al. (2008) studied the sorption of diazinon using the batch technique on two types of soil; non-modified and modified with sewage sludge and cationic surfactants. They found that "the organic matter derived from the organic cations is a more effective medium to retain dissolved contaminants, than organic matter from native soil".

Sakellarides and Albanis (2000) studied on the adsorption of organophosphorus insecticides on fly ash using batch technique. They found that "the adsorption increased with the fly ash content and reached the 100% in the "pure" fly ash. In contrast, amounts of desorbed organophosphorus insecticides decreased with increased purity of fly ash".

Kovecevic et. al. (2011) studied the adsorption-desorption of insecticide fenitrothion on organo-montmorillonite, organo-clinoptilolite and organo-sepiolite at different loadings of stearyldimethylbenzyl ammonium. They found that "the adsorption of above mentioned adsorbents for fenitrothion increased with the surfactant loading and adsorption capacities of the most hydrophobic samples was found to be greater than 89%".

1.1 The Aim of the Study

Literature survey showed that activated carbon, sepiolite, monmorillonite, clinoptilolite etc. have been used as adsorbent to remove various pollutants including some insecticides and herbicides from polluted water. This subject should be investigated in more detail to understand adsorption mechanisms and optimum parameters that determine the adsorption process.

Therefore this study has been started. In the study, zeolite and activated carbon have been used as adsorbents. Zeolite was used as received and modified by two different cationic surfactants namely, hexadecyltrimethyl ammonium bromide (HTAB) and dodecyltrimethyl ammonium bromide (DTAB). These two different adsorbents were used to remove various pesticides from solutions which are representative to wastewaters. In the examination optimum adsorption parameters, isotherms, kinetics, were determined. In addition thermodynamic parameters such as ΔG, ΔH, ΔS, and Keq were calculated.

In the second chapter, types of pesticides, their chemical compositions, pesticide cycle in nature, their effects on environment and human body, and finally usage of pesticide in World and Turkey were explained.

Third chapter contains mainly structure and properties of zeolites, geological occurrences of them, classification of zeolites, and application of them, and finally processing of methods of zeolites.

In the fourth chapter, the type of zeolite studied here (clinoptilolite) was explained in terms of crystal structure, thermal properties, and modification.

Fifth chapter contains explanation of adsorption, adsorption isotherms and their related equations.

Ion exchangers and ion exchange procedure were mentioned in chapter six.

In chapter seven materials used and experimental methods used in this study were explained.

Chapter eight contains experimental result and their discussions.

Last chapter (Chapter nine) contains conclusions deduced from the results.

CHAPTER 2

PESTICIDES

A pesticide is any substance or mixture of substances that kills a pet, or inhibits in some way its development. Under the UK Food and Environmental Protection Act of 1985, a pesticide is defined as “any substance, preparation or organism prepared or used, to protect plants or wood or other products from harmful organisms; to regulate the growth of plants; to give protection against harmful creatures; or render such creatures harmless”. A pest is some living organism that is not required in some place because of its detrimental effects (Wright, 2003).

Several hundred years ago, farmers were well familiar with both the creatures and pesticides. In order to protect their crops, they used the natural elements of the earth or heavy metals. They worked well for many years, even though these were not effective and harmful to the soil. According to Tyler (2009), the creation of synthetic pesticides began with the World Wars in the 20th century. Many scientific studies were focused onto the development and dispersal of weaponized chemical agents. Tyler (2009) indicated that “these synthetic pesticides can be used directly on specific body, such as algicides, bactericides, fungicides, herbicides, and insecticides. While in many ways these were safer than the general poisons farmer used before, the new pesticides also tended to be much more powerful. An excellent example of these early pesticides is the infamous DDT (dichlorodiphenyltrichloroethane), which is showcases both the benefits of these new pesticides and their intrinsic dangers. When DDT was first invented by a Swiss chemist, it was found to be inexpensive, potent specifically toward insects, long lasting, and insoluble” (Tyler, 2009). Saving millions of additional lives through disease vector control, its discoverer was awarded the Nobel Prize in 1948 (Spiro and Stigliani, 2003).

About 20 years after the beginning of DDT history the American author Rachel Carson published her famous book “Silent Spring” (1962). Carson presents there a dramatic picture of a world ravaged by DDT which indiscriminately brings death to people and animals (Mastalerz, 2005).

2.1 Type of Pesticides

Many different types of pesticides are available. They may be classified with respect to the target organisms, mode of action and application timing or usage (Uneke, 2007).

a) Pesticides Classification by Target Organisms

Pest can be insect, mites, mollusks, rodents, weeds, and pathogens. Various pesticides have been identified which are used to control each of these pest types. Common pesticides and their target organisms are shown in Table 2.1.

Table 2.1 Common Pesticides and Their Target Organisms

Type of Pesticide	**Target Organism**
Algicides or algaecides	Algae
Avicides	Birds
Bactericides	Bacteria
Fungicides	Fungi
Herbicides	Weeds
Insecticides	Insect
Miticides or acaricides	Mites
Molluscicides	Slugs and snails
Nematicides	Nematodes
Rodenticides	Rodents
Virucides	Viruses

b) Pesticides Classification Based on Mode of Action

Pesticides may also be classified according to their mode of action on the pest organisms as follows:

Broad spectrum: Kills broad range of pests, usually refers to insecticides, fungicides and bactericides.

Contact poison: Kills by control agent

Disinfectant: Inhibits germination of weed seed, fungus spores, and bacterial spores.

Non selective: Kills broad range of pests and/or crop plants, usually refers to herbicides

Nerve poison: Interferes with nervous system function

Protectant: Protect crops if applied before pathogens infect the crop

Repellent: Repels pests from crop or interfere with pest's ability to locate crop

Systemic: Adsorbed and translocate throughout the plant to provide protection

Stomach poison: Kills after ingestion by a pest

c) Pesticide Classification According to Application Timing

The timing of application of a pesticide is critical to its effective use. Various pests attack crops at different stages of crop production. Hence pesticides have been designed to address a pest problem at any stage of crop production as below:

Seed treatment: Pesticide coats or is absorbed into the seed

Pre plant: Pesticide applied any time before planting

At planting: Pesticide applied during the planting operation

In furrow: Pesticide applied in planting row, direct contact with crop seed.

Side dress: Pesticide applied next to the row, no direct contact with crop seed.

Broadcast: Pesticide distributer over the soil surface

Pre-emergent: Pesticide applied before the crop has emerged from the ground

Post-emerged: Pesticide applied after the crop has emerged from the ground

Lay-by: Pesticide applied during final operation before harvest sequence

Pre-harvest: Pesticide applied just before crop is harvested

Post-harvest: Pesticide applied after crop is harvested.

2.2 Chemical Composition of Pesticides

Pesticides can be classified into three main chemical groups: inorganic, organic, and microbial pesticides.

a) Inorganic pesticides: Inorganic pesticides are mineral origin. Inorganic pesticides used for pest control earlier than World War II. They are still in use, mostly for the control of plant disease. ICPAM (2006) specified that "inorganics are not very specific in their activity and are usually toxic to a wide range of organisms. They are also less effective than many of the organic compounds".

b) Organic pesticides: Organic pesticides contain carbon. They also contain hydrogen, oxygen, phosphorus, sulfur, nitrogen, or other elements. ICPAM (2006) specified that "they are extremely effective, cost-effective, easy to use, and specific in their activity". They are mainly responsible for environmental and health problems associated with pesticide use.

c) Microbial pesticides: A distinct group of pest control agent is the microbial pesticides, including bacteria, viruses, and fungi that cause disease. They are deliberately introduced in sufficient quantities to control pests, although they may occur naturally in certain areas. Their use is often called biological control. ICPAM (2006) specified that “they tend to be highly specific in their activity and are often harmless to non-target species. Only a few microbial pesticides are registered for use and their success has been limited” (ICPAM, 2006).

2.3 Insecticides

Most of the insecticides currently in use are synthetic organic compounds (Harte et. al., 1991). There are five groups of synthetic organic insecticides. These include the chlorinated hydrocarbons, organophosphates, carbamates, and synthetic pyrethroid.

a) ***Chlorinated Hydrocarbons (OCPs):*** They have been used extensively since their development in the 1940s and 1950s. Organochlorine or chlorinated hydrocarbon insecticides are part of a broad class of halogenated hydrocarbons (Harte et. al., 1991). The group include DDT and it relatives, lindane, toxophene, and cyclodiene. The organochlorines are highly persistent insecticides that are most effective against the biting and chewing insects (Agarwal, 1997). Many organochlorines are fat soluble so they can be absorbed into lipid-rich tissues and tend to accumulate in organisms. Organochlorines have long persistence time and able to accumulate in the environment. Therefore, most of them have been forbidden in most parts of the world.

b) ***Organophosphates (OPPs):*** The organophosphate insecticides were originally developed as a by-product of research into nerve gases which was carried out during World War II (Dent, 2005). Organophosphates are lees persistent therefore they do not accumulate in fatty tissues. All of the organophosphates are designed as nerve poisons. Uneke (2007) explained the mechanism of organophophates that “they block the active site of an enzyme that breaks down the removes a neurotransmitter substance from the nerve synapse”. Organophosphate insecticides have been used to control a wide range of pest insects from sheep blowfly (diazinon), locusts and grasshoppers (fenitrothion), nuisance flies such as houseflies (dichlorvos), aphids (dimethoate) and lepidopterous pest (malathion) (Dent, 2005).

c) ***Carbamates:*** Carbamates are the most widely used pesticides in the world. In the 1950s, there was interest in developing insecticides with anticholinesterase activity but reduced mammalian toxicity. As a result, several aryl esters of methylcarbamic acid were synthesized. These carbamate insecticides were synthesized as analogs of physostigmine, an anticholinesterase alkaloid extracted from the Calabar bean (Luttrell et. al., 2008). Carbaryl (Sevin) is the most widely used carbamate, it is also the least toxic to humans. Other carbamates include carbofuran, propoxur, methonyl, bendiocarb, formaetanate, oxamyl, and aldicarb (Uneke, 2007).

d) ***Synthetic pyrethroid:*** The name "pyrethrins" is applied to the crude mixture of naturally occurring pyrethroids obtained from pyrethrum extracts (Plimmer, 2001). Since it breaks down rapidly in sunlight, Pyrethrum is nearly useless outdoors. The new analogue which is light-stable was synthesized in 1967 (resmethrin).

2.4 Herbicides

Herbicide is used to eliminate unwanted plant life. Unwanted plants such as brush, weeds, unproductive bushes or trees, takes nutrients away from. Herbicides differ in how they kill plants, in the type of plants that they kill, and the amounts needed to kill plants. Herbicides may be grouped on the basis of one or more common characteristics such as chemistry (molecular composition and configuration), biological effect (mode of action, selectivity, fate in plants), method of application, or use (control of annuals, grasses, broadleaf weeds) (Datta, 1981).

a) ***Method of application*** : On the basis of method of application, herbicides are divided into:

   i. Solid surface applied: The herbicides that are surface applied or soil incorporated at pre-planting or those applied at pre-emerged of crops.

Such herbicides kill weeds at very sprouting stage in situ and crop will be free from weed competition and grow vigorously.

ii. Foliage-applied: Herbicides that are applied at post-emerged on the plant parts are included in this group. These herbicides are effective only when they are adequately adsorbed by weed flora. (Rao et. al. 2005).

b) Chemical Affinity and Structural Similarity: Herbicides which are from one chemical nucleus or family have structural similarities and affinities, provided basis for chemical classification: ex: Acetamides, Phenoxy acid types, Dinitroaniline types, etc. (Rao et. al. 2005).

i. Phenoxy Acid Type: These systemic herbicides have been widely used as brush and weed killers since the early 1950s. The primary chemicals in this class include MCPA, 2,4-D and 2,4,5-T (Donham et. al., 2006). They show a fine degree of selectivity between the susceptible broadleaf weeds and the tolerant grasses, thus facilitating their use in many cereal and grass crops (Rao, 2000).

ii. Acetamides: Acetamides (acetanilides) constitute a noticeable and diverse group of herbicides. They were first developed in the early 1950s. They are used for controlling weeds by altering protein synthesis (Hamm, 1974). The chemicals in this group include acetochlor, alachlor, butachlor, dimethenamid, metolachlor, napropamide, pronamide, propachlor, and propanil.

iii. Dinitroanilines: During the improving of dyes and dye chemical synthesis intermediates, dinitroaniline family was discovered. They are typically bright yellow in color, and are often referred to as the "yellow compounds". Trifluralin is the most important herbicide in this family which was introduced first in 1964. Dekker (2003) indicated that "trifluralin, pendimethalin, oryzalin, etc. in this family generally are used to control grassy weeds, as well as some dicot weeds like pigweeds and lambsquarters" (Dekker, 2003).

c) ***Mode of Action***: This classification of herbicides follows by means of differences in the physiological and biochemical actions of herbicides. On the basis herbicides are classified as;

i. Systemic or translocated herbicides: These herbicides require development of specific anatomical characteristic features i.e. well-developed vascular tissue throughout the plant body for effective functioning of herbicide i.e. well-formed translocation system.

ii. Non-systemic or contact herbicides: These herbicides do not require well developed translocation system; instead require effective coverage by the herbicide (Rao and Madhulety, 2005).

2.5 Fate of Pesticides in the Environment

Accidental release or agricultural application of pesticides causes the contamination of the entire habitat. Parts of the toxicants find their way into soil, surface water, sediment, ground water and the biota. The introduction of pesticides in the environment is simply depicted in Figure 2.1. This indicated that, the chemical in its original or modified form may be transported within or between environment components, cycled, or even accumulated at various stages in food chains, to levels several orders of magnitude higher than their environmental concentration (Mohapatra, 2006).

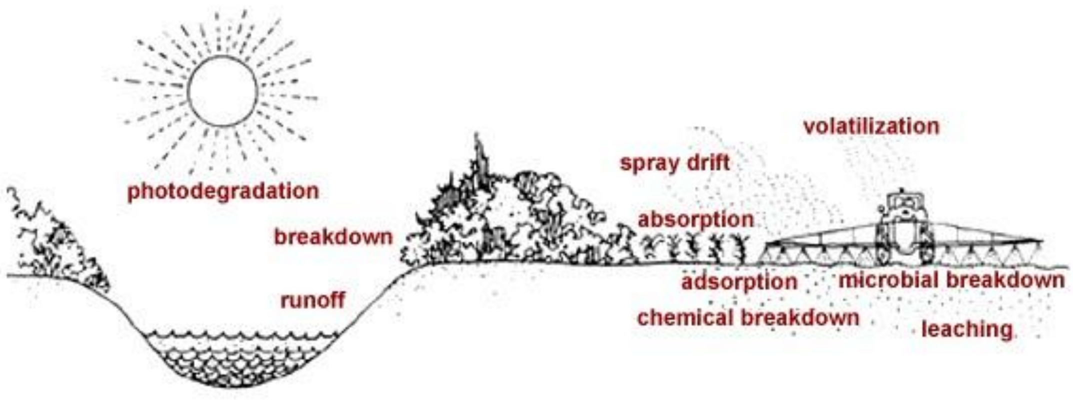


Figure 2.1 Fate Processes of Pesticide (Environmental fate of pesticide, n.d.)

In the environment, pesticides are affected by many processes. These processes are namely transfer, breakdown and degradation. Transfer processes can be defined as the processes that move the pesticide away from the target site. These processes include adsorption, volatilization, spray drift, runoff, and leaching.

Binding of pesticides to soil particles is called as adsorption. The adsorbed pesticide amount to the soil varies with the type of pesticide, soil texture, soil pH, moisture. Pesticides are strongly adsorbed to soils that are highly in clay or organic matter.

Volatilization can be defined as the conversion of a chemical substance from a liquid or solid state to a gas or vapor state. This movement is also called vapor drift. It is high when the pesticide has high vapor pressure and there is high temperature, low relative humidity and air movement.

During application, spray droplets move away from a treatment site. Geveo and Jones (2002) explained that "spray drift depends on the spray droplet size, wind speed, and distance between nozzle and target plant or ground".

Levine (2007) states that "runoff is the movement of pesticides in water over a sloping surface". The pesticides are either mixed in the water or bound to soil. When water is added to a field faster than it can be adsorbed into the soil, runoff can be occur. According to Levine (2007) "the degree of area slope, the erodibility and texture of the soil, the soil moisture content, the amount and timing of irrigation or rainfall, and the properties of the pesticide affect the amount of pesticide runoff" (Levine, 2007).

The movement of pesticides in water through the soil is called as pesticide leaching. Leaching of pesticide can be affected by several factors. Pesticides that are easily dissolved in water moves with the water as they seeps through the soil. The rate and depth of pesticide leaching can be influenced by soil structure and texture. Levine (2007) found that "Sandy and gravel soils have poor adsorption characteristics and allow water and pesticides to leach through quickly. A heavy clay soil does not allow for rapid leaching. Adsorption influences pesticide leaching because pesticides that are strongly attached to soil particles leach less" (Levine, 2007).

After adsorption of pesticides by plants or animals, pesticide residues may be decomposed in the environment or accumulate inside the plant or animal. When the animal dies or plant decays, these chemicals are feed back to the environment.

To determine the fate of the chemicals in the environment, pesticide characteristics should be known. These characteristics are:

a. Solubility in water
b. Tendency to adsorb to the soil
c. Pesticide persistence in the environment

Water solubility usually is measured in milligrams per liter of water (mg/L) or parts per million (ppm). Pesticides with high water solubility have low tendency to adsorb to soil particles.

Pesticides may also vary in their tendency to adsorb to soil particles. To measure the extent of adsorption, soil-water partition coefficient (K_D) is used, which is the ratio of the compound's concentration in soil (C_s) to its concentration in water (C_w):

$$K_D = C_s / C_w \qquad (1)$$

Soil has different physical and chemical properties; therefore K_D values are extremely site specific. In order to overcome this variability, soil-water partition coefficients are generally expressed in terms of soil organic carbon (K_{OC}) rather than total soil mass. It is the normalization of the K_D to total organic carbon content.

$$K_{OC} = K_D / f_{OC} \qquad (2)$$

Where, f_{OC} is the fraction of organic matter in soil (Weiner, 2000). Generally, K_{OC} values greater than 1000 indicate a substance that very strongly attached to the soil. Values of K_{OC} less than 500 indicate a substance that might move with water in the leaching process or move off-site with surface run-off.

Another valuable environmental characteristic of the organic chemicals is the octanol-water coefficient, K_{OW}, which is the ratio of the concentration in n-octanol (C_O) to that in water (C_W).

$$K_{OW} = C_O / C_W \tag{3}$$

A chemical that resides preferentially in the water phase is called hydrophilic; a chemical that resides preferentially in the octanol phase is called hydrophobic or lipophilic, and has a large value of K_{OW} (perhaps 10^3, 10^4, or even greater).

The water solubility of a pesticide and K_{OC} values are inversely related; pesticides that are typically not very soluble has high K_{OC} values. Similar to K_{OC} values, compounds with low water solubility has high K_{OW} and tend to partition strongly into organic-rich environmental phases, leading sorption to soil or sediments and accumulation in biota, rather than being carried by run-off or leaching (Weiner, 2000).

Half-life can be expressed as the persistence of a pesticide. It is defined as the time required for half of the pesticide present after an application to break down into degradation products. The rate of pesticide breakdown depends on a variety of factors including soil pH, soil microbe content, temperature, water, oxygen, and whether or not the pesticide is exposed to light.

Pesticides are classified into three groups based on their persistence:

a) Most Persistent (high residual): Most persistent pesticides can remain in the ecosystem between two to five years. They are adsorbed into soil particles more strongly in the presence of organic matter in the soil. Once adsorbed, they are not easily desorbed leading to poor diffusion, and poorer leaching. They are easily transported from contaminated to uncontaminated regions mainly through erosion of soil and not by diffusion. Most persistent pesticide types are grouped into two categories namely chlorinated hydrocarbons and cationic pesticides.

b) Moderately Persistent (moderately residual): Moderately persistent pesticides can remain in nature up to 18 months. Moderately persistent pesticides are grouped into three categories; triazine herbicides, phenyl urea herbicides, and substituted denitroanilines.

c) Non-Persistent (slightly residual): Non-persistent pesticides can remain in nature up to 12 weeks. Joshi (2005) grouped the non-persistent pesticides into four categories: Organophosphorous and carbamate insecticides, ethylene bisdithiocarbamate fungicides, phenyl carbamate and carbonilate herbicides (Joshi, 2005).

2.6 Effect of Pesticides

Pesticides are produced to be toxic to specific groups of organism. They can have some adverse effects on human body and environment. They are sometimes relatively obvious but often extremely subtle and complex. Some pesticides are highly specific and others broad spectrum; both types can affect environment, and humans (Pollution Issues, n.d.).

2.6.1 Effects of pesticides on humans

Pesticides are considered as poisonous to human being and animals. Pesticides are suspected of being carcinogens or disrupting endocrine activities. The results of investigation on the source of human illnesses and death over the last fifty years show that, many of them have occurred as a result of exposure to pesticides. Environmental Foundation of Turkey (1995) indicated that "if the pesticides introduced into an ecosystem do not a direct and immediate effect on certain groups of organisms, they may still have indirect toxic effect on them after some time. Pesticides may affect human beings in a number of ways: directly, through secondary toxic effects, by reducing the available types of food, by degrading the habitat, by changing the number of rival species and through problems of resistance" (EFT, 1995).

a) Direct toxic effect: When the pesticide enters the human body, either through the respiratory tract, the skin, or the mouth, the direct toxic effect of a pesticide occurs. This type of poisoning is called "acute poisoning". Delen and Tosun (1997) notified that "during the production, transportation, storage, or use of pesticides or during the consumption of the products that contain pesticide residues can cause acute poisoning". Acute toxicity is measured as an amount or concentration of a toxicant required to kill 50 % of the animals in a test population. This measure is usually expressed as LD_{50} (lethal dose) or LC_{50} (lethal concentration) (Pesticide Toxicity, n.d.).

The lower the LD_{50} (or LC_{50}) of a pesticide product, the greater its toxicity to humans and animals. Pesticides with a high LD_{50} are the least toxic to humans. World Health Organization (WHO) has classified the pesticides according to their LD_{50} values. WHO pesticide classification according to the LD_{50} values of pesticide is shown in Table 2.2

Table 2.2 WHO Pesticide Classification According to LD_{50} (2004)

WHO Class		LD_{50} for the rat (mg/kg body weight)	
		Oral	Dermal
Ia	Extremely Hazardous	< 5	< 50
Ib	Highly Hazardous	5 - 50	50 - 200
II	Moderately Hazardous	50 - 2000	200 - 2000
III	Slightly Hazardous	Over 2000	Over 2000
U	Unlikely to present acute hazard	5000 or higher	

b) Secondary effects: These refer to poisonings brought by eating either animal or vegetable foodstuffs that contain pesticide residues. Such cases are usually referred to as “chronic poisoning”. Environmental Foundation of Turkey notified that “the maximum amount of residue permitted to be found on foodstuffs for human consumption is referred to as tolerance level, and is expressed in parts per million (ppm) or in mg/kg body weight. The consumption of agricultural products with pesticide residues above tolerance level is highly dangerous for human health” (EFT, 1995). Harmancıoğlu et. al. (2001) explained that “depending on the degree of toxicity of the pesticide used against pests, certain periods of time must pass between the final application and the harvest. If the crops are harvested

> immediately following pesticide application, pesticide residues may adhere on the plant surface. Consumption of such foods may constitute serious hazards for human and environmental health" (Harmancıoglu et. al., 2001).

The health effects of studied pesticides in this work are also given in Table 2.3.

2.6.2 Effects of pesticides on environment

Use of pesticides can have undesirable effects on the environment. Most of the sprayed insecticides and herbicides reach a destination other than their target species, including non-target species, water, food, and bottom sediments. They can enter and contaminate water resources frequently by escapes, run-off, drift, erosion, and rarely, unintentional or intentional discharge. Contamination of fresh water resources is a major concern because these are used as drinking water. According to Rashid et. al. (2010) "if the half-life of a pesticide is long, aqueous solubility is high and sorption rate is low, they can contaminate groundwater gradually more. Persistence, hydrophobic nature, and bio-accumulative characteristics of a pesticide make it capable to strongly bind to soil". Most of the pesticides such as DDT, heptachlor, endosulfan, endrin, lindane, and organochlorine are currently banned for agricultural use (Rashid et. al., 2010). The environmental effects of studied pesticides in this work are given in Table 2.3.

Table 2.3 The Environmental and Health Effects of Pesticides (n.d., EXTOXNET, 2007)

Pesticide	**Environmental Effect**	**Health Effect**	**LD_{50}**
2,4 – D (Herbicide) Phenoxy group	Moderately persistent (20 - 200 days) Reduce bird hatching success, cause birth defects Destroy bird's habitat and food source Accumulate in fish	Low acute toxicity (Type III) Neuropathology (retinal degeneration) Non – Hodgkings Lymphoma (rare form of cancer) Skeletal abnormalities	LD_{50} Oral : 425 - 764 mg/kg LD_{50} Dermal: > 2000 mg/kg
Propanil (Herbicide) Acetamide	Low soil persistence (1 – 3 days) Moderately toxic to birds Highly toxic to a wide range of aquatic species	Neither carcinogenic nor mutagenic Skin and eye iritation Gastrointestinal irritation Cardiovascular problems	LD_{50} Oral : 367 - 2500 mg/kg LD_{50} Dermal: > 5000 mg/kg
Trifluralin (Herbicide) Dinitroaniline	Moderate to high persistence in the soil Trifluralin is toxic to fish and other aquatic organisms	Possible carcinogen & probable endocrine disruptor Skeletal abnormalities Liver and kidney effects Decreased weight gain, changes in hematological parameters, and increased liver weight	LD_{50} Oral : > 10000 mg/kg LD_{50} Dermal: > 2000 mg/kg
Fenitrothion (Insecticide) Organophosphate	Highly toxic to upland gamebirds Slightly toxic to waterfowl Highly toxic to honeybees	Exhausting, headache, weakness, nausea, vomiting, abdominal pain, excessive sweating. Muscle fasciculations in the face, muscle spasms, unconsciousness Difficulty in breathing and death may result from respiratory failure	LD_{50} Oral : 250 – 800 mg/kg LD_{50} Dermal: > 890 mg/kg
Diazinon (Insecticide) Organophosphate	Highly toxic to fish Highly toxic to bees	Non – Hodgkings Lymphoma (rare form of cancer) Headache, dizziness, tightness in chest, difficulty in breathing, abdominal cramps Depression, insomnia, bizarre behaviour	LD_{50} Oral : 300 – 400 mg/kg LD_{50} Dermal: > 3600 mg/kg

2.7 Pesticide Use in World

The number of people added to the world's population is increasing every year. According to UN World Water Development Report (2006), "as populations grow, the available resources per capita shrink and higher productivity is required to compensate". Production of food crops in developing countries is expected to increase by 67% to satisfy the estimated increase in demand for food between 2010 and 2030 (UN World Water Development Report -2, 2006).

Pretty (2005) states that "the use of pesticides in agriculture has increased dramatically in the past 50 years and now amounts to some 2.56 billion kg per year. The highest growth rates for the world market, some 12% per year, occurred in the 1960s. These later fell back to 2% during the 1980s, and reached only 0.6% per year during 1990s. In the early 21st century, the annual value of the global market was $25 billion, down from a high of more than $30 billion in the late 1990s. Some $3 billion of sales are in developing countries. Herbicides account for 49% of sales, insecticides 25%, fungicides 22%, and others about 3%" .

Pandya (2006) claimed that developing countries still use many of the banned or withdrawn pesticides produced in developed countries. These pesticides include DDT and other persistent organochlorine (OC) insecticides, which represent about 15% of the sales in regions outside the developed countries. Older and more toxic pesticide groups such as organophosphate (OP) and carbamate groups also have very significant sales in the Third World. According to Pandya (2006) these pesticides are still preferred by the small farmers in developing countries due to their low cost make them easily accesible, and display a wide spectrum of bioactivity (Pandya, 2006).

2.8 Pesticide Use in Turkey

There are different climates and different agro-ecologic areas, where many kinds of crop grow in Turkey (Ugurlu, 2009). Özkan et. al. (2002) state that, "agriculture contributed 11% gross domestic product and 10.7% of total exports in 2003. More than 40% of the total population is engaged in agriculture, operating 4 million farm holdings and the arable and permanent croplands makes up 30% of total land area of the country" (Özkan et. al., 2002).

Yazgan and Tanik (2003) articulated that consumption of pesticides is 50000 ton/year in Turkey. This amount includes 47% insecticides, 24% herbicides, 16% fungicides and 13% of other groups. The formally recorded data on pesticides by year 2000 represent that the number of registered pesticides used is 2000, and the number of active ingredients available is around 300. 16 of these ingredients are produced in Turkey. The rest are either directly imported or the individual formulations are imported. Yazgan and Tanik (2003) claimed that "the pesticide sales in the country are around 250 million $. However, unit pesticide consumption is still lower compared to developed countries and to European countries". This less consumption can be mainly due to economic constraints, and the agricultural policy of the Government. Meanwhile, due to the decreasing in the area of agricultural land and conversion of them into industrial districts and residential areas lead to less pesticide consumption (Yazgan & Tanik, 2003).

Because of their toxic and adverse environmental effects, and ineffectiveness, 32 different pesticides have banned to use by The Pesticide Commission of the Ministry of Agriculture and Rural Affairs within the last twenty-five years (Harmancıoglu, 2001).

Canyurt (1997) specified the amount of pesticides used in Turkey. According to Canyurt, "40% of total amount of pesticides is used the Mediterranean region in Adana, Içel and Antalya and 25% is used in Izmir, Manisa and Aydin areas" (Canyurt, 1997).

According to Pesticide Commission of the Ministry of Agriculture and Rural Affairs, the most common pesticides used in Turkey are, 2,4-Dichlorophenoxy acetic acid, propanil, diazinon, fenitrothion, and trifluralin.

CHAPTER 3

ZEOLITES

3.1 History

Swedish mineralogist Cronstedt discovered the first zeolite mineral in 1756. He recognized that zeolites as a new class of minerals consisting of hydrated aluminosilicates of the alkali and alkaline earths. Because the crystals exhibited intumescences when heated in a blowpipe flame, Crostedt called the mineral a “zeolite” derived from two Greek words, “zeo” and “lithos” meaning “to boil” and “a stone”. Damour (1840) observed that “crystals of zeolites could be reversibly dehydrated with no apparent change in their transparency or morphology”. Way and Thompson (1850) clarified the nature of ion exchange in soils. Eichhorn in 1858 showed the reversibility of ion exchange on zeolite minerals. In 1896 Friedel developed the idea that the structure of dehydrated zeolites consists of open spongy frameworks after observing that various liquids such as alcohol, benzene, and chloroform were occluded by dehydrated zeolites. Grandjean in 1909 observed that ammonia, air, hydrogen and other molecules can be adsorbed by dehydrated chabazite, and in 1925 the first molecular sieve effect was reported by Weigel and Steinhoff but McBain established the term “molecular sieve” in 1932. In 1930 Taylor and Pauling determined the first structures of zeolite.

The first classification of the known zeolite based on molecular sieve consideration was reported by Barrer in 1945. Commercially zeolites such as zeolite A, X, and Y were discovered byMilton and Breck between the 1949 and 1954. In 1954 Union Carbide commercialized synthetic zeolites as a new class of industrial materials for separation and purification.

3.2 Zeolite Framework Structures

Zeolites are crystalline aluminosilicates of group IA and group IIA elements such as sodium, potassium, magnesium, and calcium (Breck, 1974). Chemically, they are represented by the empirical formula;

$$M_{2/n}O.\ Al_2O_3\ .y\ SiO_2\ .\ w\ H_2O$$

where y is 2 to 10, n is the cation valence, and w represents the number of water molecule contained in the voids of the zeolite.

Structurally, zeolites are complex, crystalline inorganic polymers based on an infinitely extending three-dimensional, four connected framework of AlO_4 and SiO_4 tetrahedral linked to each other by the sharing oxygen ions. Each AlO_4 tetrahedron in the zeolite framework structure has a net negative charge which is balanced by a cation. Water molecules and cations occupy the zeolite channels. These cations are mobile and ordinarily go through ion exchange. The water may be removed reversibly, generally by the application of heat (Flanigen, 1991).

The structural formula of a zeolite is based on the crystallographic unit cell, the smallest unit structure, represented by;

$$M_{x/n}\ [(AlO_2)_x\ (SiO_2)_y].w\ H_2O$$

where n is the valence of cation M, w is the number of water molecules per unit cell, x and y are the total number of tetrahedra per unit cell, and y/x usually has values of 1-5. In the case of high silica zeolites y/x is 10 to 100.

3.2.1 The basic building unit: tetrahedron

All zeolite frameworks can be built by linking in a periodic pattern a basic building unit (BBU), the tetrahedron. In the center of the tetrahedra are atoms with relatively low electronegativities (Si^{4+}, Al^{3+}, P^{5+}, Zn^{2+},etc.) and in the corners are oxygen anions (O^{2-}). These combinations can be depicted as [SiO_4], [AlO_4], [PO_4], etc., and in what follows the term TO_4 to describe tetrahedra in general, where T stands for any tetrahedra species. Figure 3.1 depicts several representation of the tetrahedron.

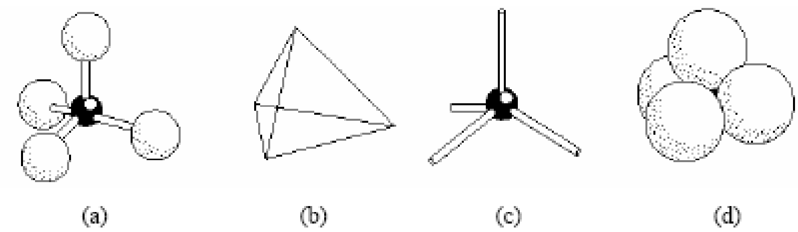


Figure 3.1 Different Representation of Tetrahedron a) Ball-and-stick Model, b) Solid Tetrahedron, c) Skeletal Tetrahedron, d) Space Filling and Packed Spheres

Each apical oxygen is shared with the adjacent tetrahedron and as a consequence the framework of zeolite materials always has a metal to oxygen ratio of 2.

The tetrahedra in zeolite materials are somewhat rigid. According to Payra and Dutta (2003) "the O-T-O angle is closed to ideal value of 109° 28′ for a geometrically perfect tetrahedron and deviations of more than a few degrees are not frequent. To build zeolite frameworks the tetrahedran are linked via the apical oxygen (T-O-T)". Payra and Dutta (2003) reported that the silica tetrahedra T-O-T angle is usually in the vicinity of 140-165°. The flexibility of the T-O-T angle is very important because it is the degree of freedom that allows the formation of the great variety of zeolite frameworks without much thermodynamic penalty. Payra and Dutta (2003) claimed that "the flexibility of the T-O-T angle allows the formation of rings and more complex building units from which zeolite material may be formed" (Payra & Dutta, 2003).

3.2.2 Composite building units

More complex composite building units (CBUs) can be formed linking together groups of BBUs. The simplest examples of CBUs are rings. All zeolite structures can be viewed as if formed of rings of tetrahedra of different sizes. In general, a ring containing *n* tetrahedra is called an *n* ring. The most common rings contain 4, 5, 6, 8, 10, or 12 tetrahedra, but materials with rings formed of 14, 18, up to 20 tetrahedra have been prepared (Meier, 1968).

This is shown schematically in Figure 3.2. Each corner in the composite building units represents the center of tetrahedron.

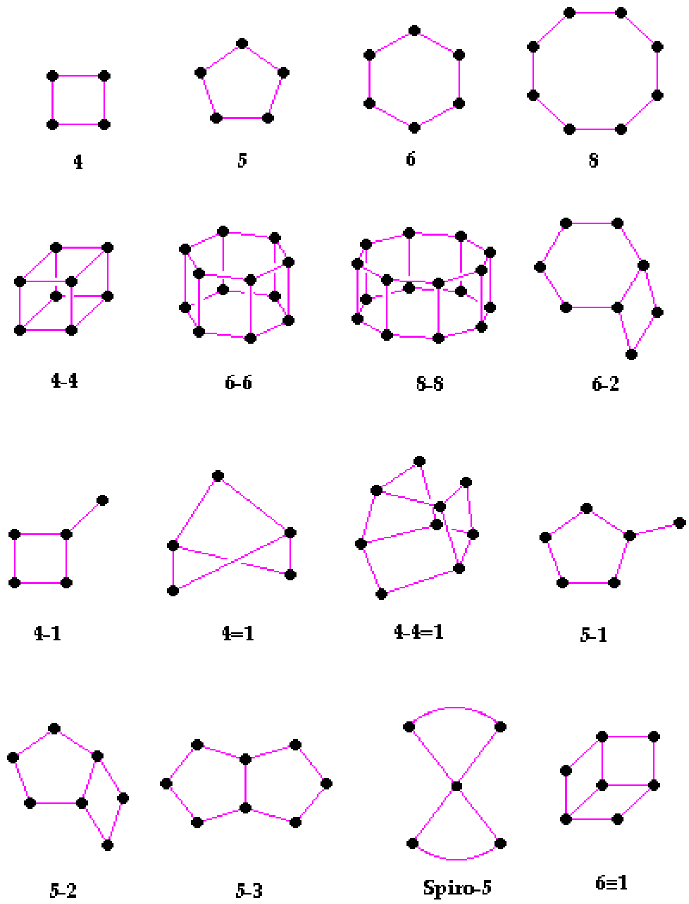


Figure 3.2 Composite Building Units (CBUs) found in Zeolites and Related Molecular Sieves.

Constructing larger CBUs from n rings give diverse and interesting set of structures such as cages whose largest rings are too narrow to allow the passage of molecules larger than water. Payra and Dutta (2003) stated that “6-rings are the limiting ring size to form a cage. Cages of different shape and geometry can be built easily connecting rings of different size. In this case, the cancrinite cage (or ε cage) and sodalite cage (or β cage) are formed connecting 4- and 6- rings in different arragments”.

These two CBUs are building units of the zeolites cancrinite (CAN) and sodalite (SOD), but they are also found in several other zeolite structures. CBUs like cages can be formally denoted by a descriptor such as $[4^6 6^5]$ (cancrinite cage) or $[4^6 6^8]$ (sodalite cage) (Figure 3.3). In the notation [$n_i^{\ m}$], m donates the number of n rings defining the polyhedron (Tsitsishvili, 1992).

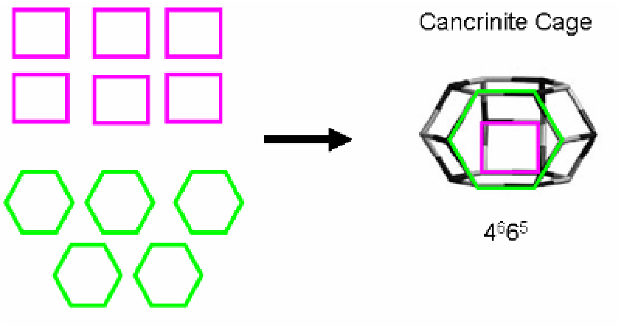


Figure 3.3 Cancrinite Cage Structure Built From Six 4-Ring and Five 6-Ring Composite Building Units (Tsitsishvili, 1992)

3.3 Cavities and channels

Cavities are polyhedral units that differ from cages by the fact that they contain windows that allow the passage of molecules in and out of the cavity. Cavities should not be infinitely extended and should be distinguished from other units such as pores and channels.

A channel is a pore that is infinitely extended in at least one dimension with a minimum aperture size (n ring) that allows guest molecules to diffuse along the pore. The aperture dimensions of a channel are qualitatively determined by the number of T atoms (or oxygen atoms) of the n-ring. Flanigen (1991) claimed that "structures with 8-ring, 10-ring, or 12-ring channel apertures are the most common and these are usually known as small-, medium-, and large-pore zeolites. Materials with 14-ring and larger channel apertures are known as extra-large pore materials" (Flanigen, 1991). Typical zeolites pore sizes using oxygen packing models are shown in Figure 3.4.

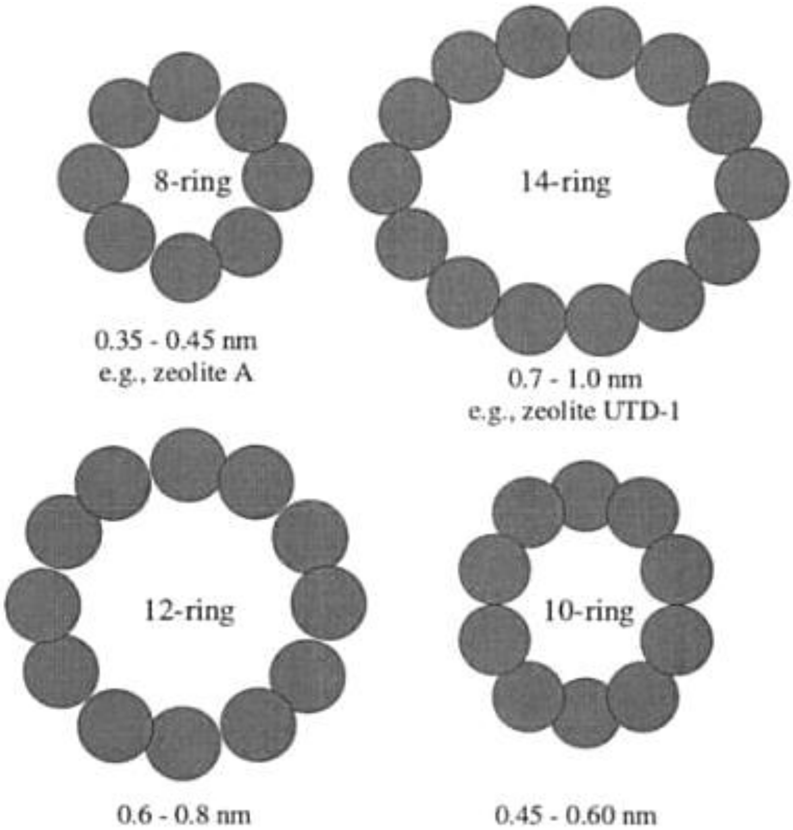


Figure 3.4 Typical Zeolite Pore Sizes Illustrated with Oxygen Packing Model (Flanigen, 1991)

In many zeolites the channels interconnect forming two- and three-dimensional channel systems. If the system is three-dimensional, a cation or molecule of appropriate size can diffuse into any available site in the crystal. If the system is two-dimensional, the molecule can only move in the plane. In the one-dimensional system, movement is possible only in one direction (Tsitsishvili, 1992). Figure 3.5 shows schematic illustrations of intracrystalline channels in zeolite.

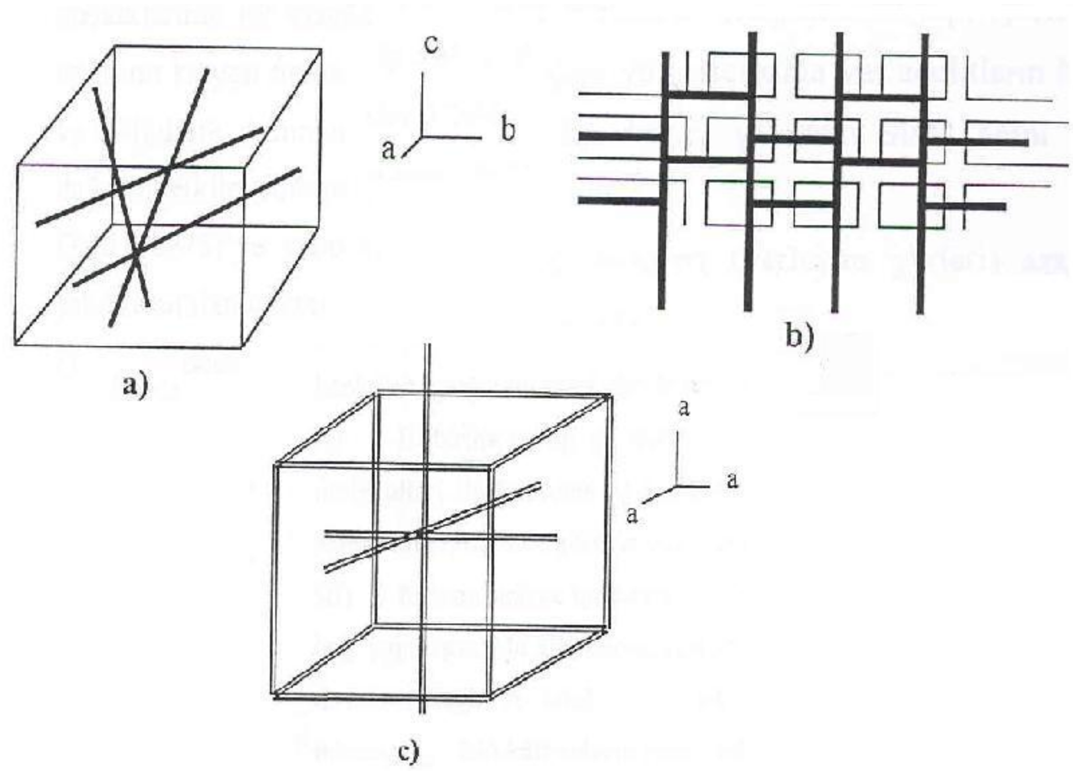


Figure 3.5 Schematic Illustrations of Intracrystalline Channels in Zeolite (a) One-Dimensional System, (b) Two-Dimensional System, (c) Three-Dimensional System

3.4 Exchangeable cations in zeolites

Cations and water molecules locate in zeolite channels and cavities under ordinary conditions (Tsitsishvili, 1992). Zeolitic water can be mobile but the cations are not free to leave the crystal structure. Barrer (1978) claimed that "cations are replaced by their electrochemical equivalent of other cations because neutralization of the anionic charge of the aluminosilicate framework must be maintained".

According to Gottardi and Galli (1985) most of the water molecules and cations occupy definite sites in the crystal lattice. Water molecules and oxygen atoms surround the cations. Gottardi and Galli (1985) also expressed that "cation-oxygen atom and cation-water molecule distances cover wide ranges and depend mainly upon the size of cation. Magnesium ions are coordinated only by water molecules, whereas potassium and barium ions are surrounded preferentially by oxygen atoms of the lattice. Coordination environments of Ca^{2+} and Na^{+} ions depend strongly upon the geometry of the cavity".

According to Gottardi and Galli (1985) the cation sites in zeolites may be classified as follows;

I. The cation is coordinated by framework oxygen only.

II. The cation is coordinated by framework oxygen at two nearly opposite sites, plus some water molecules.

III. The cation is bound to framework oxygen on one side only, plus to some water molecules.

IV. The cation is completely surrounded by water molecules.

3.5 Zeolite water

"Zeolitic water" is the water that can be removed at elevated temperature without destruction of the original structure. Zeolite water is represented in the crystals by H_2O molecules. In various structures and cation-exchanged forms, the properties and the state of this component differ. Earlier investigations compared the zeolite water with capillary or adsorbed water, and intracrystalline phases in zeolites were considered as concentrated electrolytes (the difference is that elements of the framework play the role of anions). Results of recent researches show that most water molecules, even in large cavity zeolites, occupy strictly fixed positions in the structure. As a rule, orientations of water molecules in the zeolite structure are also strictly defined.

According to structural data, H_2O – H_2O, H_2O – oxygen atom (framework) and H_2O – cation distances vary over rather wide ranges. H_2O - H_2O and H_2O – O distances are often greater than those of ice structures of crystallohydrates. In some cases cation - H_2O distances in zeolites greatly exceed the sum of the cation and water molecule radii.

According to Barrer's terminology the zeolite water is a typical guest in the host structure of the framework. According to Artioli et al. (1985) "the role of the water molecules in zeolites is twofold, to complete the coordination of the cations in the cavities and to minimize electrostatic repulsion between the framework oxygen atoms”. Belitskiy and Gabuda (1979) consider that “the role of water in the structure of zeolites is not only fill voids and distribute framework charge, but it acts as a stabilizer of the porous structure of the aluminosilicate framework” (Tsitsishvili, 1992).

According to Van Reeuwijk (1974), there are three major types of zeolitic water found in zeolite structure at room temperature; loosely held water, zeolitic water, and crystal water **(**Van Reeuwijk, 1974).

3.6 Classification of Zeolite Structures

Three classification schemes are used widely for zeolite structures. The first structural classification of zeolites is based on the framework topology, with distinct framework receiving a three-letter code (Meier et. al., 1996). The second structural method for the classification of zeolites is based on a concept termed “composite building units” (Table 3.1). The third classification scheme is similar to classification method of Breck (1974). Unlike the other two methods this classification method include historical context of how the zeolites were discovered and named. This scheme uses a combination of zeolite group names which have specific CBUs and it’s widely used by geologists (Tsitsishvili, 1992).

Another classification of zeolites is based on the structural variations as chain-like structures whose minerals form needle-like crystals (Edingtonite, Mesolite, Natrolite, Scolecite, Thomsonite), sheet-like structure where crystals are flattened with basal cleavages (Epistilbite, Heulandite, Stilbite), and framework structures where the crystals are more equal in dimensions (Analcime, Chabazite, Gmelinite, Harmotome, Levynite, Mordenite).

According to Flanigen (1991), “zeolites may be classified according to Si/Al ratio. The Si/Al ratio in natural zeolites lies within the limits of 1 to 6”. The lower limit is determined by Löwenstein’s rule, according to which an AlO_4 tetrahedron cannot associate with another AlO_4 tetrahedron by a common oxygen atom; at Si/Al =1 the silicon and aluminum tetrahedra alternate to form the ordered framework. Classification of zeolites according to Si/Al ratio is shown in Table 3.2

Table 3.1 Classification of Zeolites According to Si/Al Ratio (Flanigen, 1991)

"Low" Si/Al Zeolites (1 to 1.5)	a. Zeolite X, Zeolite A
"Intermediate" Si/Al Zeolites (2 to 5)	a. Natural Zeolites : Erionite, Chabazite, Clinoptilolite, Mordenite b. Synthetic Zeolites: Zeolite Y, L, Omega
"High" Si/Al Zeolites (10 to 100)	a. By thermo-chemical framework modification b. By direct synthesis

The low silica zeolites such as zeolites A and X are aluminum-saturated. They have the highest cation concentration therefore they have high adsorption capacity, pore size and three-dimensional channel systems. They represent highly heterogeneous surfaces with a strongly hydrophilic surface selectivity.

The intermediate Si/Al zeolites such as erionite, chabazite, clinoptilolite and mordenite, zeolites Y, omega and L are hydrophilic in this Si/Al range.

The high silica zeolites with Si/Al of 10 – 100 can be generated by either thermo-chemical framework modification of hydrophilic zeolites or by direct synthesis. These materials are reported to be hydrophobic and organophilic.

Table 3.2 Classification of Zeolites Based on CBUs (Breck, 1974; Mumpton, 1978)

Groups	Mineral	Idealized Unit Cell Composition	CBUs
1	Analcime	$Na_{16}[(AlO_2)_{16}(SiO_2)_{32}].16H_2O$	Single, 4-ring, S4R
	Harmotome	$Ba_2[(AlO_2)_4(SiO_2)_{12}].12H_2O$	
	Phillipsite	$(K,Na)_{10}[(AlO_2)_{10}(SiO_2)_{22}].20H_2O$	
	Gismondine	$Ca_4[(AlO_2)_8(SiO_2)_8].16H_2O$	
	Zeolite-P	$Na_6[(AlO_2)_6(SiO_2)_{10}].15H_2O$	
	Paulingite	$(K_2, Na, Ca, Ba)_{76}$ $[(AlO_2)_{152}(SiO_2)_{520}].700H_2O$	
	Laumontite	$Ca_4[(AlO_2)_8(SiO_2)_{46}].16H_2O$	
2	Erionite	$(Ca, Mg, K_2Na_2)_{4.5}[(AlO_2)_9(SiO_2)_{27}].27H_2O$	Single, 6-ring, S6R
	Offretite	$(K_2,Ca)_{2.7}[(AlO_2)_{5.4}(SiO_2)_{12.6}].15H_2O$	
	Zeolite-T	$(Na_{1.2}, K_{2.8})[(AlO_2)_4(SiO_2)_{14}].14H_2O$	
	Levynite	$Ca_3[(AlO_2)_6(SiO_2)_{12}].18H_2O$	
	Omega	$Na_{6.8}TMA_{1.6}[(AlO_2)_8(SiO_2)_{28}].21H_2O$	
	Sodalite	$Na_6[(AlO_2)_6(SiO_2)_6].7,5H_2O$	
	Losod	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}].19H_2O$	
3	Zeolit-A	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}].27H_2O$	Double, 4-ring, D4R
	Zeolit-N-A	$Na_4TMA_3[(AlO_2)_7(SiO_2)_{17}].21H_2O$	
	Zeolit-ZK-4	$Na_8TMA[(AlO_2)_9(SiO_2)_{15}].28H_2O$	
4	Faujasite	$(Na_2,K_2, Ca, Mg)_{29.5}[(AlO_2)_{59}(SiO_2)_{133}].235H_2O$	Double, 6-ring, D6R
	Zeolite-X	$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}].264H_2O$	
	Zeolite-Y	$Na_{56}[(AlO_2)_{56}(SiO_2)_{136}].250H_2O$	
	Chabazite	$Ca_2[(AlO_2)_4(SiO_2)_8].13H_2O$	
	Gmelinite	$Na_8[(AlO_2)_8(SiO_2)_{16}].24H_2O$	
	Zeolite-ZK-5	$(R, Na_2)[(AlO_2)_{30}(SiO_2)_{66}].98H_2O$	
	Zeolite-L	$K_9[(AlO_2)_9(SiO_2)_{27}].22H_2O$	
5	Natrolite	$Na_{16}[(AlO_2)_{16}(SiO_2)_{24}].16H_2O$	Complex 4-1, T_5O_{10} unit
	Scolecite	$Ca_8[(AlO_2)_{16}(SiO_2)_{24}].24H_2O$	
	Mesolite	$Na_{16}Ca_{16}[(AlO_2)_{48}(SiO_2)_{72}].64H_2O$	
	Thomsonite	$Na_4Ca_8[(AlO_2)_{20}(SiO_2)_{20}].24H_2O$	
	Gonnardite	Na_4 $Ca_2[(AlO_2)_8(SiO_2)_{12}].14H_2O$	
	Edingtonite	$Ba_2[(AlO_2)_4(SiO_2)_6].8H_2O$	
6	Mordenite	$Na_8[(AlO_2)_8(SiO_2)_{40}].24H_2O$	Complex 5-1, T_8O_{16} unit
	Dachiardite	$Na_5[(AlO_2)_5(SiO_2)_{19}].12H_2O$	
	Ferrierite	$Na_{1.5}Mg_2[(AlO_2)_{5.5}(SiO_2)_{30.5}].18H_2O$	
	Epistilbite	$Ca_8[(AlO_2)_6(SiO_2)_{18}].18H_2O$	
	Bikitaite	$Li_2[(AlO_2)_2(SiO_2)_4].2H_2O$	
7	Heulandite	$Ca_4[(AlO_2)_8(SiO_2)_{28}].24H_2O$	Complex 4-1-1, $T_{10}O_{20}$ unit
	Clinoptilolite	$Na_6[(AlO_2)_6(SiO_2)_{30}].24H_2O$	
	Stilbite	$Ca_4[(AlO_2)_8(SiO_2)_{28}].28H_2O$	
	Brewsterite	$(Sr, Ba, Ca)_2[(AlO_2)_4(SiO_2)_{12}].10H_2O$	

3.7 Geologic Occurrence of Zeolites

Zeolite mineral were first recognized as minor but widespread components in cavities and vugs in basalt. Big crystals can develop in these cavities through the mineralizing action of trapped or circulating solutions on the alkaline matrix, and it is these crystals which, because of their diversity of form, usually comprise zeolite collection. However, zeolite occurrences in basalt cavities were too scattered to encourage their harvesting on a large scale for industrial exploitation (Barrer, 1982). Zeolite occurrences are in no way restricted to basalt matrices, although the scale and variety of natural deposits has been appreciated only over the last two decades.

There is a remarkable connection between the chemical composition of zeolite minerals and the type of the host rock in which they are found. For example, zeolites with a low Si/Al ratio are associated with ultrabasic and basic rocks, and high silica zeolites are most often linked with acidic rocks. Analysis of geological data and experimental results shows that “all zeolites, except analcime, are formed at temperatures ranging between ambient and 250 - 300°C. The pH of zeolite-forming solutions varies from neutral to about 10”.

According to Tsitsishvili (1992), “because of the zeolites are very sensitive to changes of conditions of formation, the zonal distribution of zeolite types, even in single occurrence, reflects such gradients. As a rule, with increasing temperature or alkalinity, more hydrated, high-silica zeolites are substituted by less hydrated, low-silica species” (Tsitsishvili, 1992).

Natural zeolites occurrences may be classified into two main groups:

1. Zeolites filling veins, cracks and cavities in rocks,
2. Rock-forming zeolites.

These two groups of zeolites are formed by variable geological processes, which define composition, the dimensions of the occurrence, zonation and distribution of the minerals, etc.

3.7.1 Zeolites of vein type

Occurrences of vein type are mainly associated effusive and hypoabyssal basic to intermediate igneous rocks, but are also found in rhyolites, granites and gneisses. Zeolites fill cracks, voids and bubbles in basalts, andesites and phonolites, cement breccias, and crystallize in the inter-ball spaces of pillow leaves.

Zeolite veins are often formed via postmagmatic hydrothermal activity. The voids in recent lavas, in which fresh glass is preserved, are non-mineralized. In volcanic rocks, which contain zeolites, there is no fresh glass; it is replaced by the mineraloid palagonite, chlorite and other minerals.

Zeolites in pegmatites are of late hydrothermal origin. In acidic pegmatites, stilbite, heulandites, chabazite, laumontite, ets., are often found. For alkali pegmatites, natrolite, analcime, thomsonite and chabazite are characteristics. Stilbite is characteristic of near-surface zone, whereas laumontite is found deeper in the deposit.

In cavities in veins or geodes, the simultaneous presence of zeolite species and other minerals is frequently observed, often formed with a common paragenesis. This succession is usually explained by the Cornu rule, according to which there is a relationship between the water content of the minerals and the temperature of their formation. According to this rule, and for the main natural zeolites, the following order of crystallization is found: analcime – natrolite – mesolite – leonhardite – scolecite – thomsonite – laumontite – chabazite – heulandite – stilbite. With the rule, the distribution of zeolite minerals is definitely dependent upon the depth or the distance to a magnetic focus. The sequence envisaged by the Cotnu rule, however, is not often fulfilled. The application of the rule is restricted, since hydration effects are not only dependent on temperature, but on other formation parameters as well (changes of solute concentrations, changes of silica activity, variation of pH, etc.).

3.7.2 Occurrence of rock-forming zeolites

A limited number of zeolites are rock-forming minerals. Clinoptilolite, analcime, laumontite, mordenite, philipsite, erionite, chabazite and heulandites are widely distributed in this connection. Ferrierite, natrolite, harmotome and wellsite are less common rock-forming species. The main factors defining the mineral composition of zeolite containing rocks are the composition of the original material and the temperature and composition of the mineralizing solutions. In most cases, the original material was a glass of natural origin. Zeolitization of porous ash-glass rocks is of regional importance.

In considering the main types of occurrences of the rock-forming zeolites, classification suggested by Iijima (1978), based on temperature conditions and the nature of pores water as follows;

A. Zeolites formed at higher temperatures (Zoning is mainly caused by the temperature gradient)

    1. Magmatic primary zeolites

    2. Contact metamorphic species

    3. Hydrothermal metamorphic species

    4. Burial diagenetic or metamorphic cases

B. Zeolites formed under near-surface conditions (Zoning principally caused by chemical gradients)

    1. Percolating groundwater deposits

    2. Weathering species

    3. Alkaline, saline lake deposits

C. Zeolites formed at low temperatures (Zoning being absent)

    1. Marine environment

D. Zeolites from impact craters

    1. Impact craters

a. Magmatic primary zeolites

It has been established that the only zeolite formed at the late magmatic crystallization is analcime. Generally, analcime is precipitated interstitially between crystals of other minerals in rocks such as teschenites, analcime syenites and basalts, essexites, etc.

b. Contact metamorphisim

Occurrences of this type have been described from Japan and they are probably widely distributed in the contact aureoles of volcanic complexes, introduced into porous ashes and volcanoclastic deposits filled with pore waters.

c. Hydrothermal metamorphism

Zeolites are widespread in areas of hydrothermal alteration and may exhibit a well-defined zonation. Clinoptilolite or mordenite characterizes the shallowest and coolest zone, and progressively deeper zones commonly contain analcime or heulandites, laumontite.

d. Burial diagenesis and metamorphism

This type includes zeolite-containing rocks, formed with progressive submergence of marine or fresh water series. At the same time there are changes in the mineral and chemical composition of the sediments.

e. Percolating groundwater deposits

Zeolites are formed by the interaction of porous pyroclastic enriched with reactive glass with percolating meteoritic waters. The percolating solutions change in composition with time and this causes definite zonation. In fine grained tuff the interstitial water changes its composition by reaction with the volcanic glass. Clay minerals or palagonite are formed and the water is enriched with sodium, potassium and silica. Zeolites precipitate at certain depths when solution becomes sufficiently mineralized.

f. Weathering

Under weathering conditions zeolites are formed rarely in special circumstances. They are formed near the Earth's surface at high pH values. Saline, alkali soils are generated in semi-arid climates by concentration of sodium carbonate-bicarbonate solutions in near surface layers by evaporation of pores solution.

g. Alkaline, saline lake deposits

Zeolites are both common and widespread in deposits of saline, alkaline lakes, and vitric tuffs may alter to yield nearly pure deposits of zeolites and K-feldspar. Lake of this type are in closed basins of arid and semiarid regions. Lake water is rich in dissolved sodium carbonate-bicarbonate and has a pH of about 9.5. Trona (Na_2CO_3. $NaHCO_3.2H_2O$) is among the saline minerals that crystallize at maximum salinities. A wide variety of materials react to form zeolites in this alkaline environment, reflecting the solubility of Al and Si at high pH.

h. Marine environment

The distribution of zeolites in the ocean was only proven in the last ten years. Results of deep marine drilling gave an unexpected picture of the distribution of zeolites in the sediments of all of the oceans as well as in buried Paleozoic and Cretaceous sediments. Potassium zeolites, philipsites and clinoptilolite prevail. Harmonite, chabazite, erionite, gmelinite, laumontite, natrolite and thomsonite are found rarely.

3.8 Properties and Applications of Zeolite

Because of their special properties zeolites are used in various areas. Zeolites can interact with water to release ions; they can selectively absorb ions that fit the cavities in their structures; they can hold large molecules and help them break into smaller pieces (Payra & Dutta, 2003).

3.8.1 Applications related with adsorption

In natural zeolites, adsorption was first noted by Grandjean in 1910 and later studied by Weigel and Steinhof in 1925, Mc Bain in 1926, Sameshina in 1929, and Tiselius in

1934. Mc Bain introduced the concept of zeolites as molecular sieves in 1932 to describe the selectivity of zeolites during molecular adsorption according to size (Vaughan, 1978).

Zeolites can separate molecules based on the size and configuration of the molecule relative to the size and geometry of the main apertures of the structures. Zeolite can adsorb molecules with a selectivity that is not found in other solid adsorbents.

The most important applications related with adsorption are gas drying, and acid natural gas streams purification (Torii, 1978; Gottardi & Galli, 1985), ammonia removal from gases (Abrudean et al., 1985), air separation (Barrer, 1938; Mumpton, 1978; Triebe & Tezel, 1995), biogas purification, N_2 – O_2 separation, heat storage and refrigeration (Mumpton, 1978) and deodorization. The benefits of zeolites for these applications are heat and acid resistance, mechanical strength, higher affinity for H_2O, NH_3, and especially lower cost.

3.8.2 Applications related with ion exchange

Ion exchange is the most beneficial characteristic of natural zeolites. Ion exchange is used in aquaculture, agricultural, industrial and environmental applications of natural zeolites (Breck, 1974; Barrer, 1982).

The studies related with ion exchange were started with by Ames and co-workers (1961). They noticed that mordenite, chabazite, and clinoptilolite are the best exchangers for NH^+, Rb^+, Sr^{2+}, Cs^+, and K^+. Related studies have continued after these studies. Treatment of municipal and radioactive wastewater processes were developed (Mercer & Ames, 1978; Murphy et. al., 1978; Liberti at. al., 1995; Robinson, 1991). Similarly, there were developed agricultural (Giffiths, 1987; Torii, 1978; Pond & Yen, 1987) and aquacultural applications (Mumpton, 1978), heavy metal removal processes from wastewater (Semmens and Seyfarth, 1978; Cheslischev et al., 1974), methods for processing wastewater with high chemical oxygen demand (COD) (Sanchez & Roque, 1987), and procedures for animal nourishment (Mumpton, 1978; Tsitsishvili, 1992; Pond et. al., 1984; Castro and Pastrana, 1988).

3.8.2.1 Municipal wastewater treatment

Municipal wastewater treatment has both economic and ecological importance. The primary inorganic contaminants in municipal wastewater are ammonium and phosphate ions. Phosphates can be removed by precipitation with aluminum and iron salts whereas ammonium can be removed by using biological denitrification. For ammonium removal using of natural zeolites has been found confident. When comparison with organic ionic exchange resins, chabazite, clinoptilolite and mordenite have showed high selectivity for NH_4^+. In order to remove ammonium from wastewater, usage of zeolites as ionic exchanger has been considered.

3.8.2.2 Radioactive wastewater treatment

Radioactive materials such as Sr^{2+} and Cs^+ from solutions can be removed by using chabazite, clinoptilolite, and mordenite (Ames, 1960, 1961, 1962, 1963). Sherman (1984) found that “natural zeolites are not affected by gamma irridation and the high temperature developed by the activity of these radionuclides”. Vaniman and Bish (1995) had been studied the exchange of Th^{4+} in natural zeolite from aqueous solutions. They found that natural zeolites can be suitable barrier for the migration of radionuclides.

3.8.2.3 Heavy metals removal from wastewater

Heavy metals in water and wastewater are highly toxic on living organisms. In order to remove of heavy metals from wastewater, one of the common processes is the precipitation with lime or soda. As Colella (1995) stated “this procedure generates large amount of sludge, resulting in unacceptably high levels of residual metal salts and requiring long settling times” (Colella, 1995).

Zeolites are cationic exchangers naturally. Nowadays, it is possible to change the natural zeolites surface charge by cationic surface active agents to perform anionic exchange.

3.8.2.4 Aquaculture applications

Chabazite, clinoptilolite, and mordenite are selective for NH_4^+ exchange. One of the problems in aquaculture is the environmental contamination. In order to remove the NH_4^+ from hatchery effluent waters, clinoptilolite filters use effectively (Mumpton, 1978; Tsitsishvili, 1992; Pond et al., 1984). However, the filtering system could be expensive. Edsall and Smith (1989) offered that "natural zeolite could be added to the feed of hatchery-reared fish".

3.8.2.5 Agricultural applications

Zeolite technologies related with scientific agriculture include slow release fertilizers, zeo-ponic substrates, and soil conditioning and remediation.

In order to supply the most essential plant nutrients, mixtures of clinoptilolite and phosphate rocks have been used as active components. Yoshinaga (1973) indicated that "The slightly soluble phosphate rock serves as a P source, and the clinoptilolite act as an ion exchange and serve as both a sink for the dissolving cations and a source of nutrients such as NH_4^+ and K previously exchanged in the zeolite".

3.8.2.6 Zeolite as support material in anaerobic wastewater

Sanchez and Roque (1987) stated that zeolite can neutralize the biological media by proton exchange. During anaerobic treatment, anaerobic bacteria produce proton which increased the pH of the reactor feed.

Sanchez and Roque (1987) clarified that "zeolites used as packing material in anaerobic filters in the purification of wastewater with high volumetric organic loading are effective in decreasing its chemical oxygen demand and acidity and intensifying biogas production".

3.8.2.7 Animal nourishment

In order to increase the animal weight and feed efficiency, and to decrease frequency and severity of diarrhea, clinoptilolite can add to the food of animals such as cattle, sheep, and pigs (Mumpton, 1978; Pond et al., 1984; Castro, 1978, Castro and Pastrana, 1988). It has been suggested that "ammonium ions produced through microbial activity during the digestion of food by pigs is harmful and the reduction by ion exchange of this cation by clinoptilolite in the intestine may result in improved animal performance".

3.8.3 Applications related with catalysis

Zeolites are useful material as catalysts for several important reactions. Catalysis by hydrogen exchange zeolite is the one of the important class of reactions. Hydrogen exchange zeolite framework-bound protons give rise to very high acidity. This is abused in many organic reactions, including isomerization, fuel synthesis, and crude oil cracking. Zeolites can also serve as oxidation or reduction catalysts, often after metals have been introduced into the framework.

3.8.4 Other applications

Natural zeolites are used as fillers in some paper products, substituting for kaolin or calcium carbonate when they impart physical properties that benefit the final product (Mumpton, 1978). White clinoptilolite and mordenite have proven effective as high-bulking fillers in paper. Due to their lower brightness, they cannot compete with kaolinite and calcium carbonate for high-brightness pigment use, particularly in coating applications.

Andersson and colleagues (1975) claimed that natural philipsite has been used experimentally to separate ammoniacal nitrogen from hemodialysis liquids in recycle-dialysis systems (Andersson et. al., 1975). Clinoptilolite has been used successfully as a polishing agent in fluoride containing toothpaste, allowing the higher level of fluoride to remain in anionic form (Kato et. al., 1969, 1970).

3.9 Mining and Processing of Natural Zeolites

Clinoptilolite, mordenite, chabazite, erionite, philipsite and ferrierite rocks are mined by the open cast method, except for the Iwami deposit in Shimane Prefecture, Japan, where zeolitized dacites are mined together with polymetallic ores in underground workings. The choice of mining method depends upon geological conditions and the properties of the rocks. Zeolite rocks are soft and friable and mining is easily mechanized without use of explosives.

All consumers of zeolite rocks require the material to be crushed or ground, and in some cases they are beneficiated and pelletized. The treatment process is chosen depending upon the use of the product and the character and properties of ore.

Generally, a typical process includes crushing with intermediate sieving. After a first crushing the material is dried (in air or in ovens). It is expedient to grind to a uniform size. This is usually achieved in a ball or vibrating mill without addition of grinding agents. Major production methods for zeolite are shown in Figure 3.6.

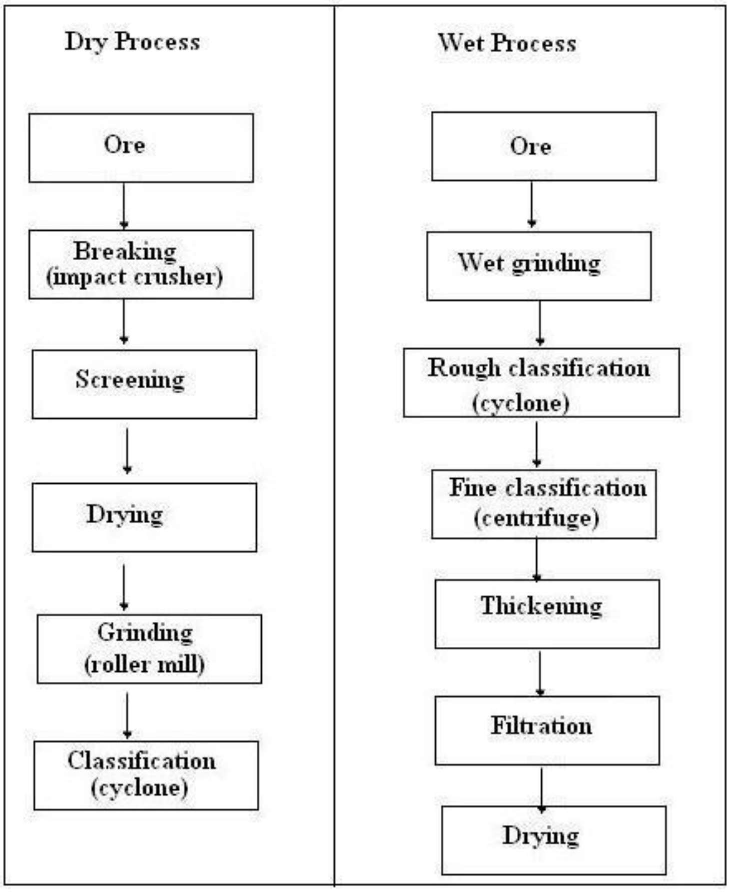


Figure 3.6 Major Production Methods for Zeolite

CHAPTER 4

CLINOPTILOLITE

4.1 Crystal Structure

The relative merits of the clinoptilolite and heulandites have received much attention since Mumpton (1978) proposed differentiation on the basis of Si / Al ratio and thermal stability, and Mason and Sand (1960) forwarded the alternative view that relative levels of monovalent and divalent cations should be the deciding factor.

According to Mason and Sand (1960), both Si/Al ratios and cation contents determine the properties of zeolites. The Si/Al ratios of zeolites vary from about 2.7 for heulandites to about 5.3 for clinoptilolite. Calcium, sodium, and potassium are the major cations. Lower Si/Al ratio heulandites have high calcium content and higher Si/Al ratio clinoptilolites have high potassium content (Mason & Sand, 1960).

Alietti (1972) and Boles (1972) investigated the relationships between chemical composition and thermal behavior, so clarifying the differences of the two zeolites. Boles (1972) proposed naming these zeolites clinoptilolite if Si/Al > 4, heulandite if Si/Al < 4. Zhao and colleagues (1998) investigated the zeolite thermal behavior and they found that “clinoptilolite is thermally stable to temperatures in excess of 500°C, while heulandite undergoes structural collapse by 350°C” (Zhao et. al., 1998).

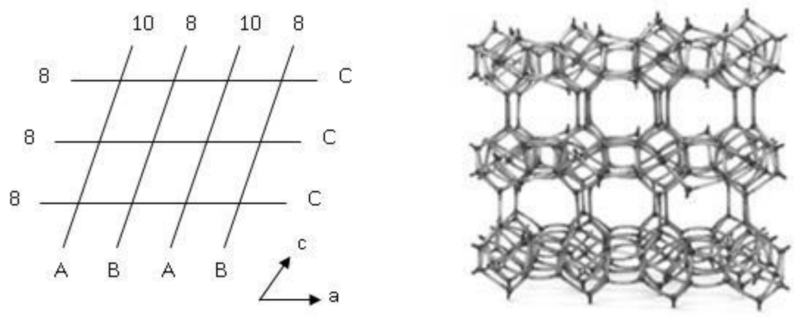
Clinoptilolite can be represented by typical oxide formula as

$$(Na_2, K_2)O \,.\, Al_2O_3 \,.\, 10\, SiO_2 \,.\, 8\, H_2O$$

Unit cell contents of clinoptilolite can be represented as:

$$(Na, K)_6 . (Al_6Si_{30}O_{72}) . 24 H_2O$$

Clinoptilolite is assigned to the same framework HEU (heulandite) in which 4-4-1 secondary building units. These units are linked together to form a two dimensional channel structure with elliptical pore openings. Channel A (10-membered ring) and B (8-membered ring) are parallel to each other and the c axis of the unit cell, while the C channel (8-membered ring) lies along a axis, intersecting both the A and B channels as shown in Figure 4.1 (Ackley and Yang, 1991a). Small hydrated cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) can easily enter the channels of clinoptilolite and compete for the major exchangeable cation sites, designated as M(1), M(2), M(3), and M(4). The cation site M(1) is located in channel A, coordinated with two framework oxygen and five water molecules. This site is occupied by Ca^{2+} and preferably by Na^+. M(2) is located in channel B, coordinated with three framework oxygen and five water molecules. M(2) is occupied by Na^+ preferably by Ca^{2+}. M(3) is located in channel C, coordinated six framework oxygen and three water molecules. This site is occupied by K^+ and preferably by Ba^{2+}. Because this position is very close to M(1) a simultaneous occupancy of both sites is not possible. M(4) is located in the center of channel A different from M(1). It is coordinated by six water molecules forming an octahedral system and occupied by Mg^{2+} (Koyama & Takeuchi, 1977). Channel characteristics and cation sites of clinoptilolite are summarized in Table 4.1 (Ackley and Yang, 1991b).



(a) (b)

Figure 4.1 Intersection of A and B Channels, (a) Orientation of Clinoptilolite Channel Axes. (b) Model Framework for the Structure of Clinoptilolite

Table 4.1 Channel Characteristics and Cation Sites in Clinoptilolite (Ackley and Yang, 1991b)

Channel	Tetrahedra ring size / Channel axis	Cation site	Major cation	Approximate channel dimension (A° x A°)
A	10 / c	Na, Ca	M(1)	7.2 x 4.4
B	8 / c	Ca, Na	M(2)	4.7 x 4.1
C	8 / a	K	M(3)	5.5 x 4.0
A	10 / c	Mg	M(4)	7.2 x 4.4

4.2 Crystallographic properties

The unit cell of clinoptilolite is monoclinic and is usually characterized on the basis of 72 oxygen atom and 24 water molecules, with Na^+, K^+, Ca^{2+}, and Mg^{2+} as the most common charge-balancing cations. Representative unit cell parameters are: a : 17.62 A°, b : 17.91 A°, c : 7.39 A° , and β: 2.029 rad (Figure 4.2).

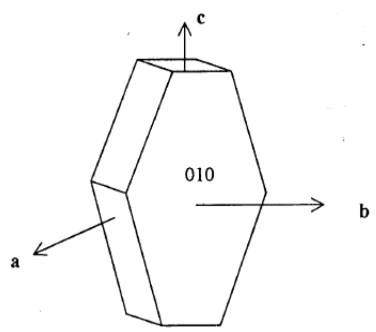


Figure 4.2 Clinoptilolite Unit Cell Parameters

4.3 Thermal properties

There are important factors in determining the macroscopically observable thermal effects (e.g., evolution of H_20, decrease in volume, and structural breakdown or modification). These factors include the amount and type of extra-framework cation (i.e., its ionic potential), the Al/Si ratio, the connectivity of the structure (e.g., "flexibility"), the presence or absence of H_2O, and the time, temperature, and rate of heating.

Van Reeuwijk (1974) classified water in zeolites into three categories based on calorimetrically measured heats of dehydration: loosely held water, zeolitic water, and crystal water. Knowlton and White (1981) classified water in clinoptilolite as externally adsorbed, loosely bound zeolitic water, and tightly bound zeolitic water. Van Reeuwijk anticipated recent studies by concluding that low-entropy ("crystal") water is associated with cations occupying fixed positions in structural channels and high-entropy ("zeolitic") water is associated with cations that cannot be located at specific fixed positions. Zeolitic water is typically used to describe H_20 molecules that can move freely in and out of the structure without disrupting it.

Bisehke et al. (1988), Bish (1988), and Armbruster (1993) investigated the H_20 molecules on zeolite and they found that "H_20 molecules are held with a pseudocontinuous range of energies, and furthermore, this range of energies is a function of temperature". As some H_20 molecules evolve at lower temperatures, remaining H_20 molecules are attracted more strongly to extra-framework cations. Thus, H_20 evolution occurs in a pseudocontinuous but stepwise manner, with H_20 evolving from specific sites, often with concomitant migration of extra-framework cations and subsequent structural relaxation (Armbruster and Gunter, 1991; Armbruster, 1993). According to Bish (1988), the externally adsorbed water in zeolites does not held in the same manner as water adsorbed on the surfaces of materials. As the H_20 in structural cavities is linked with extra-framework cations, the dehydration of zeolite is strongly dependent on the extra-framework cations, in particular their hydration energy. Zeolites containing high hydration-energy cations (such as Ca^{2+} (M2) and K^+ (M3)) contain more H_20 than those containing low hydration-energy cations (such as Na^+ (M1)) and those with high hydration-energy cations also generally retain their H_20 to higher temperatures (Bish, 1988).

4.4 Modification of clinoptilolite structure

Zeolite framework composition and its pore structure identify the zeolite properties and functions. Xu et al (2007) defined that "the framework composition is a reflection of the Si/Al ratio, which is highly related with the thermal and hydrothermal stability, the chemical stability, the adsorption properties, the acidity and the catalytic activity of the zeolites. In general, a zeolite with high Si/Al ratio is more able to resist heat, water vapor, and acid. With increase of Si/Al ratio, the surface hydrophilicity and hydrophobicity vary accordingly, leading to variation of adsorption properties of zeolite" (Xu et. al., 2007)

The catalytic, sorptive and ion-exchange properties, and in particular the chemical and thermal stability, of zeolites depend strongly on the tetrahedra aluminum content in the framework. It is, therefore, of particular interest to modify the Si/Al ratio of the zeolite while retaining the topology and crystallinity of the framework structure (Engelhardt, 1991). In General, there are three kinds of dealumination methods. These are;

a) High temperature dealumination and ultra-stabilization: The Na-zeolite with a certain Si/Al ratio is exchanged with NH_4^+. The ammonium salts such as ammonium sulfate, ammonium nitrate, ammonium chloride can be used for exchange.

   According to Xu et. al. (2007) "when the Na^+ content in the zeolites with low Si/Al ratio reaches 10-25%, it is difficult to exchange more sodium ions by NH_4^{+}". They reduced the Na_2O content in the zeolite to 4% with calcination (at 200-600°C) and exchanged with NH_4^+. In this way, the Na^+ cations in Na-zeolite move from the unexchangeable sites to the exchangeable ones. NH_4^+ decomposes with high temperature. By heating ammonium zeolite to 260 °C, H-type zeolite can be formed. H^+ has strong polarizing ability; therefore it can form hydroxyl with the zeolite framework oxygen. At high temperatures, these hydroxyls can be removed as water. Xu et. al. (2007) found that "dealumination through calcination of NH_4^+ -zeolite to above 500 °C leads to structure destruction. Therefore high temperature calcination of NH_4^+ -zeolite alone cannot be used to obtain dealuminated product. Usually it requires high temperature water-vapor treatment of NH_4^+ -zeolite to achieve dealumination and framework structure stabilization" (Xu et. al., 2007).

b) Chemical dealumination route: Dealumination of zeolites can be performed by using inorganic and organic acids. The amorphous species that are blocking the channels usually are dissolved by the acid. Chemical dealumination procedure decreases the stacking defects. Proceeding of zeolite with acid brings about pore size expansion and adsorption capacity improvement by replacing of the small radius protons with the larger radius cations. Acid treatment of zeolites with low Si/Al ratio is unsuitable because this will generate a large amount of hydroxyl nests and will lead to lattice destruction.

c) Gas-solid reactions: In order to remove aluminum from zeolite, gas solid reactions can applicable. Reactions can be performed by using F_2, $COCl_2$. The $SiCl_4$ reaction method is the most commonly used for dealumination and silicon enrichment among the gas-solid reactions.

CHAPTER 5

ADSORPTION

Adsorption can be defined as binding of molecules of substances at a surface or interface. The process can occur at an interface between any two phases, such as liquid-liquid, gas-liquid, gas-solid, or liquid-solid interface. The material being concentrated or adsorbed is the adsorbate, and the adsorbing phase is termed the adsorbent.

Depending on the type of bonding, adsorption can be classified as follows;

a. Physical adsorption (Physisorption): In physical sorption, no exchange of electrons is observed. The adsorbate is held to the surface by weak van der Waals forces and multiple layers may be formed with approximately the same heat of adsorption. According to Inglezakis and Poulopoulos (2006) the heat of physisorption is at most a few kcal/mole and therefore this type of adsorption is stable only at lower temperatures. Everett and Koopal (1971) characterized some features of physisorption. These are;

1. Physisorption occurs in any solid/fluid system arising from particular geometrical or electronic properties of the adsorbent and/or adsorptive;
2. The adsorbed species are chemically identical with those in the fluid phase. Therefore the chemical nature of the fluid is not changed by adsorption and subsequent desorption;
3. The interaction energy between the molecules of adsorbate and the adsorbent is of the same order of magnitude as the energy of condensation of the adsorptive;

b. **Chemical adsorption (Chemisorption):** In chemical adsorption, specific surface sites electrons exchange with solute molecules; and as a result a chemical bond is formed. Chemisorption is much stronger and more stable than physisorption. According to Inglezakis and Poulopoulos (2006), only a single molecular layer can be adsorbed in chemisorption. Some features which are useful in recognizing chemisorption are as follows (Everett and Koopal, 1971):

1. Changes in the electronic state may be measurable by suitable physical paths
2. The chemical nature of the adsorptive may be changed by surface disassociation. Original species cannot be recovered by desorption.
3. The chemisorption energy is of the same order of magnitude as the energy change in a chemical reaction between a solid and a fluid
4. The basic step in chemisorption often involves activation energy; where the activation energy for adsorption is large, true equilibrium may be achieved slowly or in practice not at all.
5. As the adsorbed molecules are linked to the surface by valence bonds, they will usually occupy certain adsorption sites on the surface and only one layer of chemisorbed molecules is formed.

c. **Electrostatic adsorption (Ion exchange):** In electrostatic adsorption, Coulomb attractive forces are formed between ions and charged functional groups. Electrostatic adsorption is commonly classified as ion exchange.

5.1 Factors influencing adsorption

5.1.1 Surface area

Adsorption is surface phenomenon; therefore the extent of adsorption is proportional to specific surface area. Weber (1972) defined the surface area that "portion of the total surface area that is available for adsorption". According to Crank (1956), adsorption rate should exhibit a monotonic increase with some function of the inverse of diameter of the adsorbent particles. Crank (1956) stated that "if the mechanism of uptake is one of adsorption on external sites of a nonporous adsorbent, the rate should vary reciprocally with the first power of the diameter for a given mass of adsorbent. This inverse relationship holds also for porous adsorbents when the rate of transport to internal surface areas is controlled by an external resistance, that is, film transport. Conversely, for cases in which intra-particle transport controls the sorption rate, the variation should be with the reciprocal of some higher power of the diameter" (Crank, 1956).

5.1.2 Nature of adsorbate

The solubility of the solute is a controlling factor for adsorption equilibrium. Generally, there is opposite relationship between the extent of adsorption of a solute and its solubility in the solvent from which adsorption occurs.

Solubility-adsorption relationships can be explained by postulating the necessity of breaking some form of solute-solvent bond before adsorption can occur. The greater the solubility, the stronger the solute-solvent bond and the smaller the extent of adsorption.

A general rule for the effect of solute polarity on adsorption is that a polar solute will prefer the phase which is more polar. In other words, a polar solute will be strongly adsorbed from a non-polar solvent by a polar adsorbent, but will much prefer a polar solvent to a non-polar adsorbent. Polarity of organic compounds is a function of charge separation within the molecule. The solubility of any organic compound in water decreases with increasing chain length. This forms the basis for the second major statement regarding the relationship between adsorption and the nature of the solute (Traube's rule).

5.1.3 pH

The pH of a solution from which adsorption occurs may influence the extent of adsorption. Because hydrogen and hydroxide ions are adsorbed quite strongly, the adsorption of other ions is influenced by the pH of the solution. Weber (1972) claimed that "adsorption of typical organic pollutants from water is increasing with decreasing pH. In many cases this may result from neutralization of negative charges at the surface of the adsorbent with increasing hydrogen ion concentration, thereby reducing hindrance to diffusion and making available more of the active surface of the adsorbate" (Weber, 1972).

5.1.4 Temperature

Weber (1972) stated that “adsorption reactions are normally exothermic; thus the extent of adsorption generally increases with decreasing temperature”. The heat of adsorption, ΔH, is termed as the change in the heat content of a system in which adsorption occurs. According to Weber (1972), parameter ΔH can be defined as the temperature dependence of equilibrium capacity for adsorption and E_a (activation energy) can be defined as the rate of adsorption.

5.1.5 Adsorption of mixed solutes

In the wastewaters, the material wanted to be removed commonly will be a mixture of many compound rather than single one. The compounds may mutually enhance adsorption, may act relatively independently, or may interfere with one another. Mutual inhibition of adsorption capacity can be predicted to occur provided: adsorption is confined to a single or a few molecular layers, the adsorption affinities of the solutes do not differ by several orders of magnitude; and there is not a specific interaction between solutes enhancing adsorption.

5.2 Adsorption isotherms

The adsorption phenomenon gives valuable information on the physical and chemical properties of a solid surface and is represented by adsorption isotherms. In the case of vapor-solid system, the isotherm is usually expressed by the relationship between the adsorbed amount (V) and the equilibrium vapor pressure (P) of an adsorbate at a fixed temperature (T).

$$V = f_T \,.\, (P) \tag{4}$$

On the other hand, in the case of a liquid-solid system, concentration I of adsorbate in a solution is used instead of vapor pressure.

$$V = f_T \,.\, I \tag{5}$$

The other expressions obtained at a fixed pressure or at a constant amount of adsorbed molecules are given as follows (Chikazawa & Takei, 2006).

$$V = f_P \,.\, (T) \tag{6}$$

$$V = f_V \,.\, (T) \tag{7}$$

The experimentally observed adsorption isotherms can be classified (Figure 5.1) according to IUPAC-recommendations in 6 different types

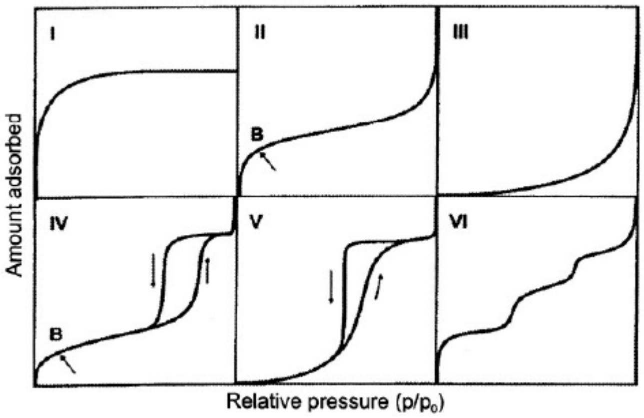


Figure 5.1 Types of Adsorption Isotherms (IUPAC, 1985)

Lowell et. al. (2004) explained the adsorption isotherms as follows;

"The reversible type I isotherm can be easily explained by using Langmuir adsorption isotherm. Type I isotherms are obtained when adsorption is limited to only a few molecular layers. This condition is encountered in chemisorption, where the asymptotic approach to a limiting quantity indicates that all of the surface sites are occupied. In the case of physical adsorption, sorption isotherms obtained on microporous materials are often of type I. Micropore filling and therefore high uptakes are observed at relatively low pressures, because of the narrow pore width and the high adsorption potential. The limiting uptake is being governed by the accessible micropore volume rather than by the internal surface area.

Type II Adsorption Isotherm shows large deviation from Langmuir model of adsorption. Type II sorption isotherms are typically obtained in case of non-porous or macroporous adsorbent, where unrestricted monolayer-multilayer adsorption can occur. The inflection point or knee of the isotherm is called point B. This point indicates the stage at which monolayer coverage is complete and multilayer adsorption begins to occur.

Type III adsorption isotherm also shows large deviation from Langmuir model. The reversible type III isotherm is convex to the P/P_o axis over its entire range and therefore does not exhibit a point B. This indicates that the attractive adsorbate-adsorbent interactions are relatively weak and that the adsorbate-adsorbent interactions play an important role.

Type IV isotherms are typically for mesoporous materials. The most characteristic feature of this type IV isotherm is the hysteresis loop, which is associated with the occurrence of pore condensation. The limiting uptake over a range of high P/P_o results in a plateau of the isotherm, which indicates complete pore-filling. The initial part of the type IV can be attributed to monolayer-multilayer adsorption as in case of the type II isotherm.

Type V isotherm shows pore condensation and hysteresis. However, in contrast to type IV the initial part of this sorption isotherm is related to adsorption isotherms of type III, indicating relatively weak attractive interactions between the adsorbent and the adsorbate.

Type VI isotherm is a special case, which represents stepwise multilayer adsorption on a uniform, non-porous surface, particularly by spherically symmetrical, non-polar adsorptive. The sharpness of the steps depends on the homogeneity of the adsorbent surface, the adsorbate and the temperature" (Lowell et. al., 2004).

5.3 Adsorption equations

In specific system, a substance adsorption from one phase to another leads to a thermodynamically defined distribution of that substance between the phases when the system reaches equilibrium. This distribution can be expressed as the amount of substance adsorbed per unit weight of adsorbent, q_e, as a function of the residual equilibrium concentration, C_e, of substance remaining in the solution phase. Adsorption isotherm defines the functional equilibrium distribution of adsorption with concentration of adsorbate in solution at constant temperature.

By using experimental isotherms, the feasibility evaluation of process for a given application can be described, most appropriate adsorbent can be selected, and adsorbent dosage requirements can be determined. Besides, in order to predict the modeling procedure for analysis and to design the adsorption systems, the experimental isotherms are used (Weber & Crittenden, 1975; Mathews & Weber, 1977; Crittenden & Weber, 1978a, b, c). In general, the adsorption isotherm describes how adsorbates will interact with adsorbents (Juang et al., 1997). Several equilibrium models have been developed to describe adsorption isotherm relationship.

5.3.1 Langmuir equation

This model originally developed for adsorption of gases onto solids. Langmuir equation is predicated on the some assumptions. According to these assumptions, adsorption energy is constant and independent of surface coverage. This means that adsorption occurs on localized sites with no interaction between adsorbate molecules. Maximum adsorption occurs when the surface is covered by a monolayer adsorbate (Langmuir, 1918).

The linearized Langmuir isotherm is represented by following equation

$$C_e / q_e = 1/ Q_oK_L + C_e / Q_o \tag{8}$$

Where C_e is the liquid phase concentration at equilibrium (mg/L), q_e is the amount of the solute adsorbed per unit weight of adsorbent (mg/g), K_L is the Langmuir adsorption constant (L/mg), Q_0 is the solid phase concentration corresponding to complete coverage of available sites (mg/g) (Weber, 1985).

The isotherm can be classified by a term “R_L”, a dimensionless constant separation factor, which is defined as below in equation.

$$R_L = 1 / (1 + K_LC_o) \tag{9}$$

The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L= 1$), favorable ($0 <R_L < 1$), or irreversible ($R_L = 0$) (Juang et al., 1997).

5.3.2 Freundlich equation

Freundlich isotherm equation is assumed to have a heterogeneous surface consisting of sites with different adsorption potentials. According to Freundlich isotherm, each type of sites is assumed to adsorb molecules (Perry & Green, 1984).

The Freundlich equation has the general form

$$q_e = K_F.\ C_e^{\ 1/n} \tag{10}$$

where K_F and n are constant, and n > 1.

The Freundlich equation is basically empirical but is often useful as a means for data description. Data are usually fitted to the logarithmic form of the equation;

$$\log q_e = \log k_f + \log C_e / n \tag{11}$$

5.3.3 BET Equation

Brunauer, Emmett, and Teller (1938) extended the Langmuir model to include multi-layer adsorption phenomena under a few assumptions (Weber, 1985). According to Weber (1985), the essential assumptions of the BET equation are that "any given layer need not be complete before subsequent layers can form, that the first layer of molecules adheres to the surface with energy comparable to the heat of adsorption for monolayer attachment, and that subsequent layers are essentially condensation reaction". From these assumptions, the BET equation is obtained;

$$V = \frac{V_m C X}{(1-X)(1-X+CX)} \tag{12}$$

where X is the relative vapor pressure P/P_O, C is the value related to the strength of adsorption force, P_o is the saturated vapor pressure at measurement temperature, and V_m is the monolayer capacity. If the adsorbed layer is restricted to the *n*th layer, the BET equation becomes

$$V = \frac{V_m C X\left[1-(n+1)X^n+nX^{n+1}\right]}{(1-X)\ [1+(C-1)x-CX^{n+1}]} \tag{13}$$

CHAPTER 6

ION EXCHANGE

An ion exchange reaction was defined by Harland (1994) as “the reversible interchange of ions between a solid phase (the ion exchange) and a solution phase, the ion exchanger being insoluble in the medium in which the exchange is carried out”. If an ion exchanger M^-A^+, carrying cations A^+ as the exchanger ions, is placed in an aqueous solution phase containing B^+ cations, an ion exchange reaction takes place which may be represented by the following equation:

$$M^-A^+ + B^+ \rightarrow M^-B^+ + A^+$$

Above equation represented that an example of cation exchange, where M^- is the insoluble fixed anionic complement of the ion exchanger M^-A^+. The cations A^+ and B^+ are referred to as counter ions, whereas ions in the solution which bear the same charge as the fixed anion of the exchanger are called co-ions. In the same way, anions can be exchanged provided that an anion-receptive medium is employed. An anion exchange reaction may be written (Harland, 1994):

$$M^+A^- + B^- \rightarrow M^+B^- + A^-$$

According to Helfferich (1962), ion exchange looks like sorption in that, in both cases, a dissolved species is taken up by a solid. According to Helfferich (1962), ion exchange is a stoichiometric process which is opposite of adsorption. The differences between the ion exchange and adsorption are that every ion removed from the solution is replaced by an equivalent amount of another ionic species of the same sign.

Whereas in sorption, a solute is taken up without being replaced by another species (Helfferich, 1962).

6.1 Ion Exchangers

Ion exchangers are insoluble solid materials. They carry exchangeable cations or anions. When the ion exchanger is in contact with an electrolyte solution, exchangeable cations or anions can be exchanged for a stoichiometrically equivalent amount of other ions of the same sign. Carriers of exchangeable cations are called cation exchangers and carriers of exchangeable anions, anion exchangers (Helfferich, 1962). Ion exchangers can be either naturally occurring inorganic zeolites or they can be synthetically produced organic resins. The synthetic organic resins are the major type used today. In general, according to Liberti and Helfferich (1983), the ideal ion exchanger should have;

- Thermal, chemical and physical stability
- Controlled and effective ion exchange capacity
- Hydrophilic structure of regular and reproducible form
- Consistent particle size compatible with hydraulic design requirements
- Rapid rate of exchange

6.1.1 Inorganic Ion Exchangers

Most natural ion exchange minerals are crystalline alumina silicates with cation exchange properties. Characteristic representatives of this group of materials are the zeolites which have a relatively open three-dimensional framework structure with channels and interconnecting cavities in the lattice. The zeolite lattice consists of SiO_4 and AlO_4 tetrahedra which have their oxygen atoms in common. Since aluminum is trivalent and silicon is tetravalent, the lattice carries a negative electric charge. This negative charge is balanced by alkali or alkaline earth cations. These cations do not occupy fixed positions, but are free to move in the channels of the lattice framework and they act as counter ions and can be replaced by other cations.

Other alumina silicates with cation exchange properties have a loose layer structure. They carry their counter ions in between the layers of the lattice. Characteristic minerals of this type are montmorillonite and beidellite. These materials can swell in one dimension by increasing their interlayer distance (Helfferich, 1962).

Harland (1994) and Helfferich (1962) investigated the nature of ion exchange reactions, and they found important conclusions some of the more important ones being

1. Exchange involved equivalent quantities of ions.
2. Certain ions were more easily exchanged than others.
3. The temperature coefficient for the rate of exchange was small.
4. The alumina silicate fractions of soils were responsible in the main for the exchange although these components rarely took part in the exchange itself.
5. Material possessing exchange properties could be synthesized from soluble silicates and aluminum sulfate.

There are similarities between zeolites and clay minerals. Both classes of materials are mineral in origin, comprising similar elements. Water is also an important component in both types of minerals. Both have an intrinsic ability to exchange cations, and this intrinsic ability arises as a consequence of isomorphous replacement. Zeolites are similar to clay minerals in another respect, in that an ion exchange capacity can arise not from an intrinsic property which occurs as a consequence of isomorphous substitution in the framework, but rather from unsatisfied valencies occurring at the crystal edges and faces, or from faults within the structure. The most common origin of an ion exchange capacity arising as a consequence of such faults, dislocations or edges comes from the presence of silonol groups or hydroxyls attached to edge aluminums. Townsend stated that “in clay minerals up to 20 % of the exchange capacity may arise from these sources; in the case of zeolites the extent of exchange capacity arising from such sources is normally small relative to the intrinsic one" (Townsend, 1991). Harland (1994) reviewed the characteristic ion exchange properties of the alumina silicates extensively. According to Harland (1994) typical exchange capacity values, in equivalents per kilogram, or eqkg $^{-1}$ are shown in Table 6.1 (Harland, 1994).

Table 6.1 Typical Cation Exchange Capacities of Some Silicate Minerals (Harland, 1994).

Structural Type	Mineral	Cation Exchange Capacity (eqkg-1)
Single Layer	Kaolinite	0.03 – 0.15
	Halloysite (2H2O)	0.05 – 0.10
	Liversite	0.40
Double Layer (non-expanding lattice)	Muscovite (mica)	0.10
	Illite (hydrous mica)	0.10 – 0.40
	Glauconite	0.11 – 0.20
	Pyrophyllite	0.04
	Talc	0.01
Double Layer (expanding lattice)	Montmorillonite	0.70 – 1.00
	Vermiculite	1.00 – 1.50
	Nontronite	0.57 – 0.64
	Saponite	0.69 – 0.81
Three Dimensional (dense lattice)	Feldspar (Orthoclase)	0.02
	Quartz	0.05
Open Lattice	Zeolites	4-6.0

6.1.2 Organic Ion Exchangers

Many substances of an organic nature were examined but the first real success was with sulfonated coals around 1900. Certain types of soft coal, when treated with hot fuming sulfuric acid, reacted partially to give sulfonic acid groups ($-SO_3H$) on the hydrocarbon matrix. The sulfonic acid groups conferred a measure of hydrophilic nature so that when placed in aqueous solution the material is ionized according to the equation:

$$R(SO_3H)_n \overset{H_2O}{\Longleftrightarrow} [R(SO_3)_n]^{n-} + nH^+$$

where R represents the hydrocarbon matrix, and n is the number of fixed ionizable sulfonic acid groups carried on the matrix. Thus the hydrogen counter ions are able to exchange for cations in the external solution. These materials were termed 'carbonaceous' exchangers or 'carbonaceous zeolites' from which the trade name 'Zeo-Karb' was coined by The Permutit Company in the 1930s. This class of exchanger lacked uniformity, physical and chemical stability, and possessed about one third the total ion exchange capacities of modern resins. Yet with all these shortcomings they were in use as cation exchangers in industrial water treatment applications until as late as the mid-1970s (Harland, 1994).

The early cation exchange resins prepared by B. A. Adams and E. L. Holmes in 1935 were obtained by the condensation of tannins and phenol with formaldehyde; the anion exchange resins were made by condensing aniline or metaphenylene diamine with formaldehyde. These early resins were not very stable chemically and tend to dissolve in alkaline solution. More recently, however, ion exchange resins based on styrene polymers have been developed which have a high chemical and physical stability.

Ion exchange resins may be regarded as insoluble acids or bases which also form insoluble salts. They consist of a cross linked polymer network to which are attached ionized or ionizable groups. The resins swell in water but the cross links between the polymer chains prevent them from dissolving either in water or other solvents. Each particle of an ion exchange resin can therefore be regarded as 'giant molecule'. The functional groups can ionize into a fixed ion, which is attached to the polymer chain and is immobile, and a counter ion, which is mobile and can diffuse through the swollen resin and exchange with an ion of like charge in a surrounding solution. Cation exchange resins contain acidic groups, e.g., SO_3H, COOH, or phenolic OH groups. According to Salmon and Hale (1959), "they can be classified as strongly acidic resins or weakly acidic resins depending on the nature of the acidic group.

Anion exchange resins contain either strongly basic quaternary groups, e.g., $N(CH_3)_3OH$ or weakly basic groups, e.g., NH_2, $NHCH_3$, or $N(CH_3)_2$" (Salmon & Hale, 1959).

6.2 Ion Exchange Procedures

Three techniques are used for the practical application of ion exchange: batch operation, column processes and continuous processes.

Batch operation is the simplest ion exchange process. The adsorbent is contacted with the adsorbate in any desired vessel until exchange equilibrium has been established between the counter ions of the adsorbent and the ions of equal charge of the adsorbate. The degree to which this process takes place depends on the equilibrium constant of the ion exchange system. After equilibrium has been attained, the ion exchanger is filtered (Dorfner, 1972).

The column process is the most frequently used laboratory technique. The ion exchanger is packed in a glass column and all necessary operations are carried out in this bed. Fundamentally, two techniques can be distinguished here, the descending and the ascending flow process. In the first case, the liquid moves down and in the second, up through the exchanger bed (Dorfner, 1972).

In the continuous ion exchange processes, the exchanger and liquid usually move in counter current columns. It is a characteristic and disadvantage of column process that a large part of the upper ion exchange bed remains in the column without utilization during the run, while the lower part performs the ion exchange. The logical theoretical consequence of this fact is that the exhausted part of an ion exchange column should be continuously removed and regeneration performed immediately, and this already establishes the characteristic feature of the continuous or fluid bed process (Dorfner, 1972).

CHAPTER 7

MATERIALS AND METHODS

In this chapter, materials used and the methods applied in the study were explained separately.

7.1 Materials Used

The zeolite used in this study was clinoptilolite ($(Na, K, Ca)_{2-3} Al_3 (Al, Si)_2 Si_{13} O_{36} .12 H_2O$). It was taken from Rota Mining Corporation in Manisa-Gördes region. In the experiments the zeolite was ground and passed through 80 μm sieve, washed with deionized water, dried in an oven at 100 ± 10 °C for 24 h and kept in a desiccator until use. Activated carbon was supplied from Calgon Carbon Corporation. Characteristics of activated carbon are as follows; particle size in the range of 0.55-0.75 mm and BET surface area 750 m^2/g.

Insecticides and herbicides used as pesticides were purchased from Sigma-Aldrich Company. Types of pesticides and their physico-chemical properties are listed in Table 7.1.

Organic cations used to prepare organo-zeolite are quaternary alkyl ammonium compounds namely Hexadecyltrimethyl ammonium bromide (HTAB) and Dodecyltrimethyl ammonium bromide (DTAB). They were obtained from Merck Chemicals Company. Their chemical properties are shown in Table 7.2.

Other reagents used through the study were listed in Table 7.3.

Table 7.1 Physical and Chemical Properties of Pesticides

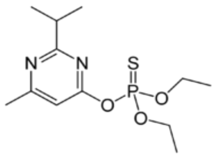
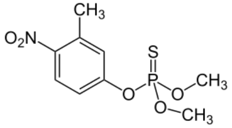
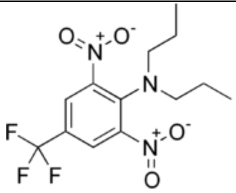
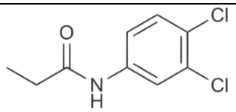
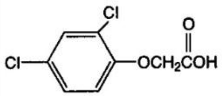
Pesticide Name	CAS Number	Chemical Structure	Formula	Mol.Wt (gr/mol)	Solubility (mg/L)	Log K_{ow}	pK_a	UV (ads. Val.) (nm)
DIAZINON (Insecticide)	333-41-5		$C_{12}H_{21}N_2O_3PS$	304.35	60	3.69	-	246.8
FENITROTHION (Insecticide)	122-14-5		$C_9H_{12}NO_5PS$	277.23	30	3.32	-	272
TRIFLURALIN (Herbicide)	1582-09-8		$C_{13}H_{16}F_3N_3O_4$	335.28	24	5.27	-	237.2
PROPANIL (Herbicide)	709-98-8		$C_9H_9Cl_2NO$	218.08	225	2.29	-	248.95
2,4 – D (Herbicide)	94-75-7		$C_8H_6Cl_2O_3$	221.04	900	2.81	2.64-3.31	282.8

Table 7.2 Chemical Properties of Cationic Surfactants

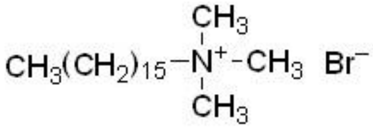
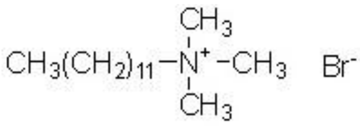
Cationic Surfactant	Open Structure	Chemical Formula	Mol. Wt. (g/mol)
Hexadecyl trimethyl ammonium bromide (HTAB)		$C_{19}H_{42}NBr$	364.45
Dodecyl trimethyl ammonium bromide (DTAB)		$C_{15}H_{34}NBr$	308.34

Table 7.3 Reagents Used in Experiments

Reagents	**Formula**	**Description**
Hydrochloric acid	HCl	1.15 g/cm^3, % 30
Sulfuric acid	H_2SO_4	1.84 g/cm^3, % 96
Phosphoric acid	H_3PO_4	1.27 g/cm^3, % 42.5
Disulphine Blue	$C_{54}H_{62}CaN_4O_{14}S_4$	1159.45 g/mol
Dimidium Bromide	$C_{20}H_{18}N_3Br$	380.3 g/mol
Chloroform	$CHCl_3$	1.48 g/cm^3
Ethanol	C_2H_5OH	0.805 g/cm^3, % 96
Sodium dodecyl sulphate	$C_{12}H_{25}NaO_4S$	288.38 g/mol

7.2 Methods Used

In this section, analysis techniques and instruments used for characterization of materials will be explained.

7.2.1 X-Ray Diffraction Analysis (XRD)

XRD examinations were performed on powder zeolite samples to verify the mineral identity. The analysis was carried out with RIGAKUD/MAX diffractometer (CuKα - Ni Filter) in General Directorate of Mineral Research and Exploration. The X-Ray generator worked at a power of 40 kV and 40 mA. X-ray traces were obtained for 2θ values from 5° - 50°.

7.2.2 X-Ray Fluorescence Spectroscopy (XRF)

X-Ray Fluorescence analyses were performed to determine the elemental composition of zeolite sample by using SPECTRO IQ X-Ray Fluorescence in METU Mining Engineering Department. Sample was prepared by using the pressed powder technique with binder (a certain wax).

7.2.3 Differential Thermal Analysis (DTA)

DTA was carried out to determine the thermal behavior of the materials using SETARAM - Simultaneous Thermogravimetric Analyzer (TG) and Differential Thermal Analyzer (DTA). The powders of the zeolite sample were heated in a dry N_2 stream up to 1200 °C at a heating rate of 10 °C/min.

7.2.4 Specific Surface Area & Pore Size Distribution Analysis

The BET specific surface area and pore size distribution analysis of zeolite was done via an automated gas sorption system (QUANTACHROME Autosorb Automated Gas Sorption System) using N_2 gas as adsorbate in METU Central Laboratory.

7.2.5 Electro-kinetic Analysis

The electrokinetic properties of as-received and modified zeolite sample were examined by using MALVERN Zetasizer. Before measurement, 1 g of material was mixed with 100 ml of distilled water for 10 minutes using a shaker. The surface charge of zeolite was determined at pH values varying from 2 to 12. In the experiments, pH was adjusted by using 0.1 M HCl and 0.1 M NaOH. The suspension was kept for 5 minutes to allow the larger particles to settle down. Each data point corresponds to average of 10 measurements.

7.2.6 Spectroscopic Analysis

The amount of pesticide adsorbed from solution was determined by using PERKİN-ELMER LAMBDA 3B Ultraviolet Double-Beam Spectrophotometer in Michigan Tech. Uni., Dep. of Material Science, Mineral Processing Lab., and SHIMADZU UV-1601 Ultraviolet Spectrophotometer in METU Mining Engineering Department.

7.2.7 Scanning Electron Microscopy (SEM)

Scanning electron microscopic analyses were carried out to investigate the morphology of as-received zeolite and activated carbon by using QUANTA 400F Field Emission instrument in METU Central Laboratory. Analyses were performed on high-resolution scanning electron microscope at 10 kV with a working distance of 9.3 mm. Samples were coated with a very thin layer of a gold-palladium (Au-Pd) alloy to make the surfaces conductive.

7.2.8 Scanning Electron Microscopy /Energy Dispersive X-Ray Analysis (SEM-EDX)

An EDX coupled with SEM allows determining the chemical composition of material by measuring the X-rays emitted during the electron-specimen interaction. Quantity of main elements such as Si, Al, Fe, Ca, Mg, Na and K were determined.

7.2.9 Fourier Transform Infrared Spectroscopic Analyses (FTIR)

Fourier transform infrared spectroscopic analysis was performed to identify the chemical bond types of organo-zeolite by using Thermo Scientific Nicolet IS10 FT-IR spectrometer with a Smart ITR diamond ATR device in Chemistry Depertment of METU.

7.3 Sequence of Experiments

7.3.1 Activation of Zeolite Structure

Activation of zeolite had been carried out in two ways. One of them is acid activation and the other one is thermal activation.

The zeolite lattice consists of SiO_4 and AlO_4 tetrahedra which have their oxygen atoms in common. Since aluminum is trivalent and silicon is tetravalent, the lattice carries a negative electric charge. This charge is balanced by alkali or alkaline earth cations. These cations do not occupy fixed positions but free to move in the channels of the lattice framework. These exchangeable cations placed within the framework play a critical role in ion exchange ability of zeolite.

Ion exchange ability and surface properties of zeolite are changed by Si/Al ratio. High silica zeolites are more hydrophobic and acid stable. They have less ion exchange capacity whereas low silica zeolites are hydrophilic, acid soluble, and having higher ion exchange capacity. In highly concentrated acid aqueous solutions, zeolite loses some of its Al^{3+} ions (dealumination) in the lattice. When the degree of dealumination becomes higher, crystal structure of zeolite may collapse.

In this study, an inorganic acid (HCl, and H_2SO_4) with different molarities were used to dissolve amorphous species that are blocking the channels and decreases the staking defects. The acid treatments of zeolite were performed by treating 100 ml inorganic acids with different molarities with 50 g of zeolite sample for 24 h. After treatment, the solid remains were filtered from solution. Residues were washed with distilled water until a negative test for chloride ion (in the case of HCl) was observed using $Ag(NO)_3$, or a negative test for sulfate ion (in the case of H_2SO_4) was observed using $BaCl_2$. After that, samples were dried in air at room temperature.

From the DTA pattern of the zeolite, it can be seen that zeolitic water was removed until 200°C and structural breakdown was occurred up to 900°C. Therefore, thermal activation of zeolite was carried out between the temperatures 100°C-500°C. Adsorption studies of cationic surfactants on thermally activated zeolites were performed by keeping the concentration of cationic surfactants and solid amount fixed as $1x10^{-3}$ M and 5 g respectively. The results from the adsorption studies indicated that, 300°C was the optimum activation temperature.

Changes on zeolite structure were determined by XRD and XRF analyses.

7.3.2 Modification of Zeolite Structure

Zeolite structure was modified using quaternary alkyl ammonium compounds. Activity (capacity) of these compounds was examined using two-phase titration method (DIN EN 13435).

This test method includes a titration procedure to determine active matter in disinfectant quaternary ammonium salts. In this titration method, the reaction involves the formation of a compound between the quaternary ammonium cation ($R-N^+$ or $R^{'}-N^+$) and the anion of a surfactant ($R^{''}-SO_3^-$) which then precipitates.

Cationic surfactants react with the system of disulphine Blue – dimidium Bromide indicator to form a blue chloroform-soluble complex, while anionic surfactants react with the same indicator system to form a pink chloroform-soluble complex.

When a solution containing a cationic surfactant is titrated with a standard solution of an anionic surfactant, the chloroform layer changes from blue to pink at the end point.

Solutions of cationic surfactants used namely HTAB and DTAB were prepared using powder of the surfactants dissolved in distilled water.

Preliminary studies showed that 5×10^{-4} M surfactant concentration is the best concentration for them.

Similarly, for anionic surfactant previous studies showed that 1×10^{-3} M is the best concentration for it.

The stock indicator solution was prepared by mixing 0.1 g dimidium bromide, 0.05 g disulphine blue, 5 mL ethanol, and 45 mL distilled water.

The indicator solution used in titration was prepared by mixing 10 mL stock solution with 1.4 mL H_2SO_4 and distilled water until total volume become 500 mL.

In the analysis standard procedure (DIN EN 13435) was followed.

The sample was prepared as follow;

5 g of zeolite is mixed with 100 mL of $5x10^{-4}$ M a cationic surfactant for 24 h at room temperature using a shaker. Then the suspension was centrifuged at 400 rpm. After centrifugation supernatant was decanted into 100 mL graduated cylinder. This procedure was done using two different cationic surfactants.

Indicator solution was prepared by mixing 20 mL stock indicator solution and 15 mL chloroform in a beaker.

In the analysis 3 mL sample was taken using a pipette and put into the indicator solution given above and mixed well.

Titration is done with $1x10^{-3}$M anionic surfactant (SDS – sodium dodecyl sulfanate) until the Chloroform layer changes from blue to pink. This point was decided as end point.

7.3.3 Adsorption Experiments

Experiments related with adsorption on zeolite were divided into two parts. First part was adsorption of quaternary alkyl ammonium on activated zeolite (acid activated and thermal activated) which is called organo-zeolite and the second part was pesticide adsorption on organo-zeolite.

7.3.3.1 Adsorption of Quaternary Alkyl Ammonium Compound on Activated Zeolite

Routine adsorption experiments were performed by the batch technique. Batch technique is a simple phase contacting technique. Here adsorbent (organo-zeolite, natural zeolite) is made in contact with solution of any kind of substance such as cationic surfactant, anionic surfactant and so on. In practice, 5 g zeolite was placed in 100 mL surfactant solution.

Effects of initial concentration of cationic surfactants, time, temperature, and pH were investigated. Amount of quaternary alkyl ammonium compound in the supernatant was determined by using two-phase titration method.

In order to obtain relevant data for adsorption kinetic a fixed amount of adsorbent (5 gr) was shaken with 100 mL of the surfactant solution for the time between 10 - 300 min at constant temperature. The entire batch tests were performed in glass bottles in duplicate and average values was used in the calculation.

7.3.3.2 Adsorption of Pesticides on Organo-Zeolite

The stock solutions of pesticides were prepared on the basis of their solubility in water. Effects of initial concentration of pesticides, time, temperature, and pH on adsorption of organo-zeolite were investigated by using again batch method. Each suspension was stirred at speed of 400 rpm for varied time period. After a definite time, the solids were removed from the pesticide solutions by filtration. Then UV-Vis. spectra of the solutions were obtained. Adsorption studies were repeated three times and average values were used in the calculations.

CHAPTER 8

RESULTS AND DISCUSSION

8.1 Characterization of Zeolite Structure

Characterization of zeolite was done by various analyses which are given below.

8.1.1 Chemical Analysis of the Zeolite

In the XRD traces characteristic peaks of clinoptilolite of 9.1681 A°, 3,9750 A°, 3.4338 A°, 2.9852 A°, and 2.8087 A° were observed (Fig 8.1). Beside these, quartz and heulandite peaks were also seen.

XRF analysis showed that natural zeolite samples (clinoptilolite) have 75.68 % SiO_2, 14.23 % Al_2O_3, 0.68 % Na_2O, 2.19 % K_2O, 3.55 % CaO, 1.60 % MgO, 1.70 % Fe_2O_3 and remaining 0.351 % for other elements such as Ti, P, S.

Si/Al mole ratio of zeolite was calculated from the result of XRF analyses as 4.52, which is within typical limits (4-5.25) for clinoptilolite (Boles, 1972).

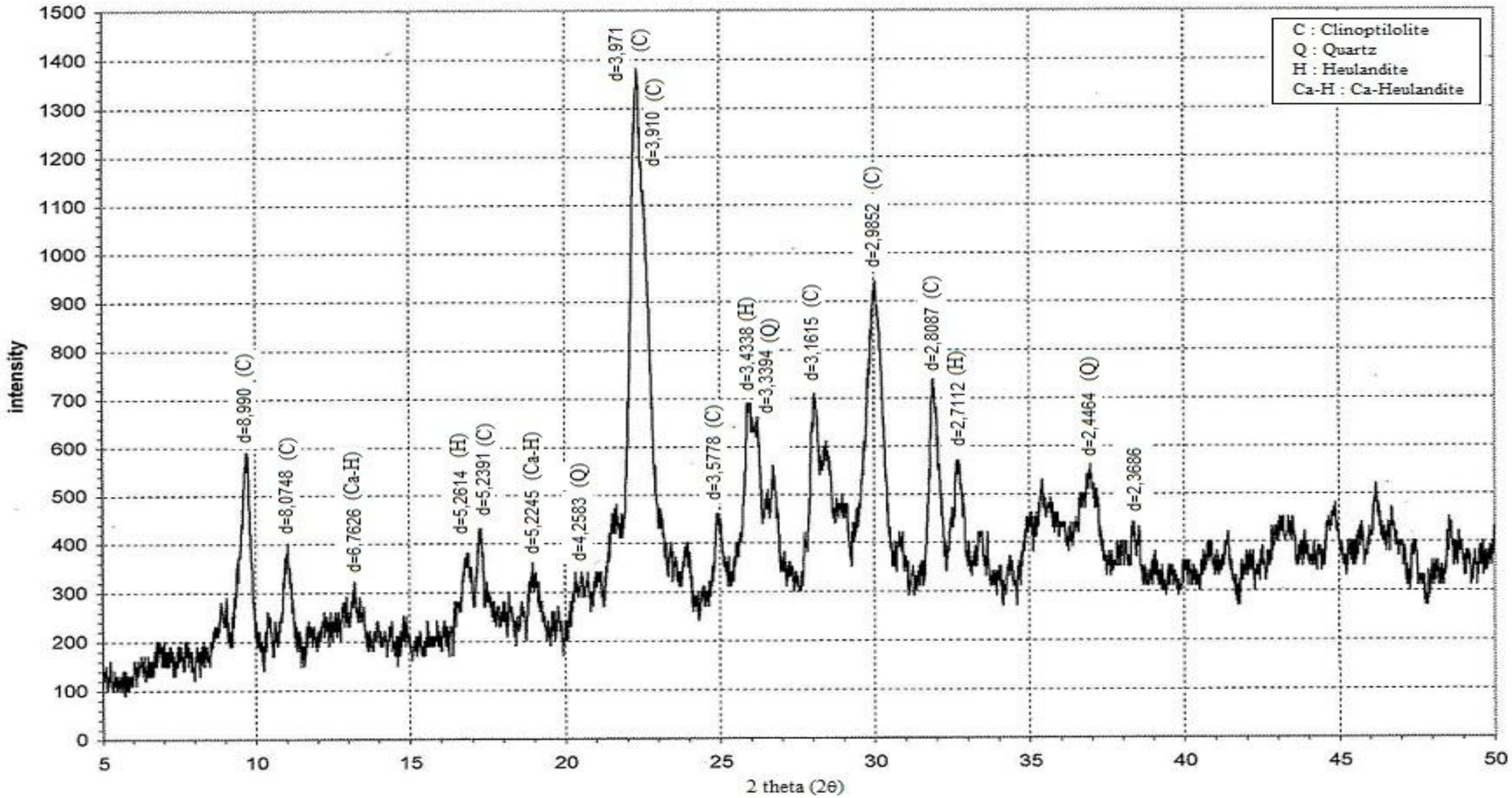


Figure 8.1 The XRD Pattern of Original Test Sample

According to results, theoretical cation exchange capacity of (TCEC) the clinoptilolite is 2.76 meq/g, which was calculated as the sum of Na^{+}, K^{+}, Ca^{2+}, and Mg^{2+} content of clinoptilolite. The contribution of each exchangeable ion to the exchange capacity are 0.22 meq Na^{+} /g (7.96 %), 0.468 meq K^{+} /g (16.94 %), 1.27 meq Ca^{2+} /g (46.01 %), 0.8 meq Mg^{2+} /g (29 %).

The results of chemical composition of as-received zeolite sample obtained from SEM/EDX analysis is showed in Figure 8.2. Chemical compositions obtained from XRF and SEM/EDX analysis are mostly the same. Average pore diameter, density, and surface area of zeolite were calculated as 0.041 μm, 2.10 g/cm^3, and 40.79 m^2/g respectively.

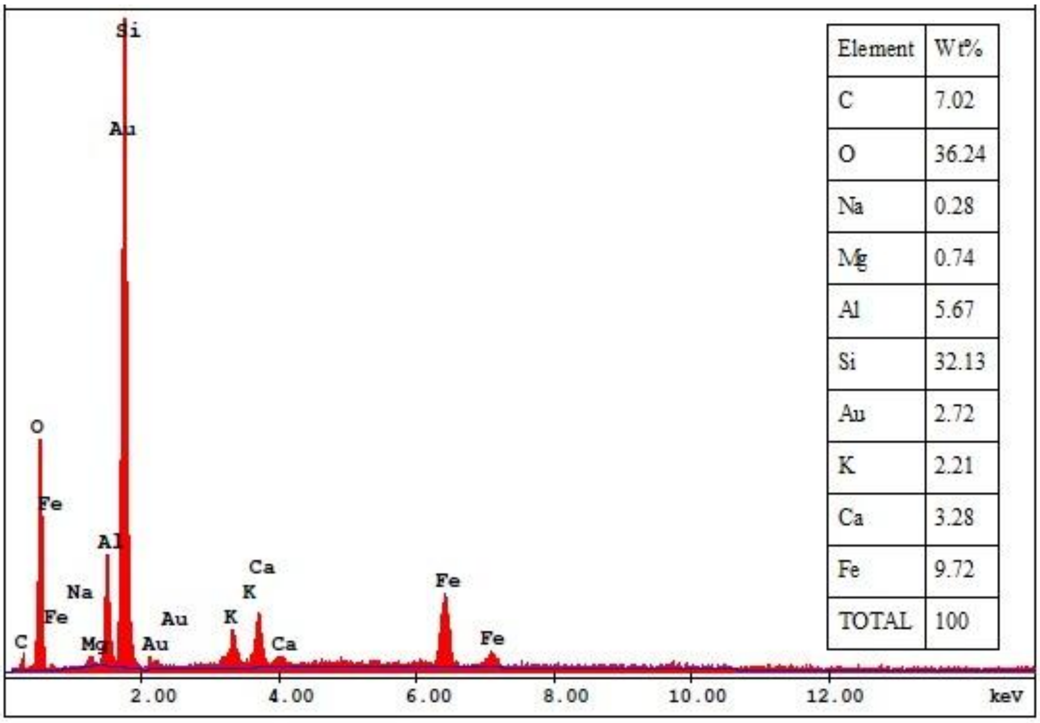
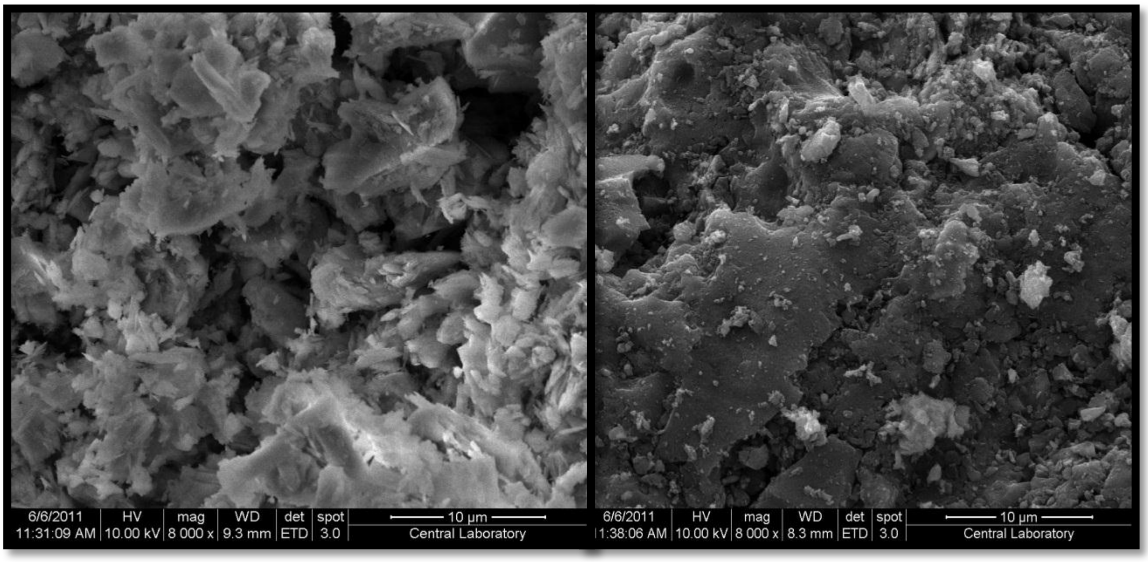


Figure 8.2 Chemical Analysis of Zeolite Samples Performed with SEM/EDX

8.1.2 Scanning Electron Microscopy (SEM) Analysis

SEM micrographs of as-received zeolite and activated carbon are given in Figure 8.3. As shown in Figure 8.3(a), typical coffin-shaped crystal structure of clinoptilolite was observed although not clear enough, and Figure 8.3(b) shows that activated carbon has amorphous structure as expected.



(a) (b)

Figure 8.3 Scanning Electron Microscopy (a)Clinoptilolite, (b) Activated Carbon

8.1.3 Thermal Properties of the Zeolite

Thermal properties of zeolite samples are important in thermal activation zeolite structure which needs temperature range for the activation process.

Thermal behavior of zeolite was investigated by using TG and DTA. The TG curve of the zeolite showed that external water of zeolite has released up to 150 °C, and loosely bound water was lost rapidly up to 200 °C. After 200 °C zeolite started to loss it’s tightly bound water, and above 800 °C not considerable weight loss takes place in the structure. After 1000°C, 15.4% of its weight was lost.

DTA determines the temperature at which thermal reaction takes place within the sample. The degree and the nature of the reactions that is whether endothermic or exothermic are obtained from analysis curve. The low temperature endotherm represents the loss of water while the high temperature endotherm represents conversion of the zeolite to another amorphous or crystalline phase. The high temperature exotherm represents the loss of structure (Breck, 1974). The DTA pattern of the sample shows that zeolitic water was dehydrated until 200°C and a broad exothermic peak was observed between 300 °C and 900 °C, which gives information on the structural breakdown (Figure 8.4.).

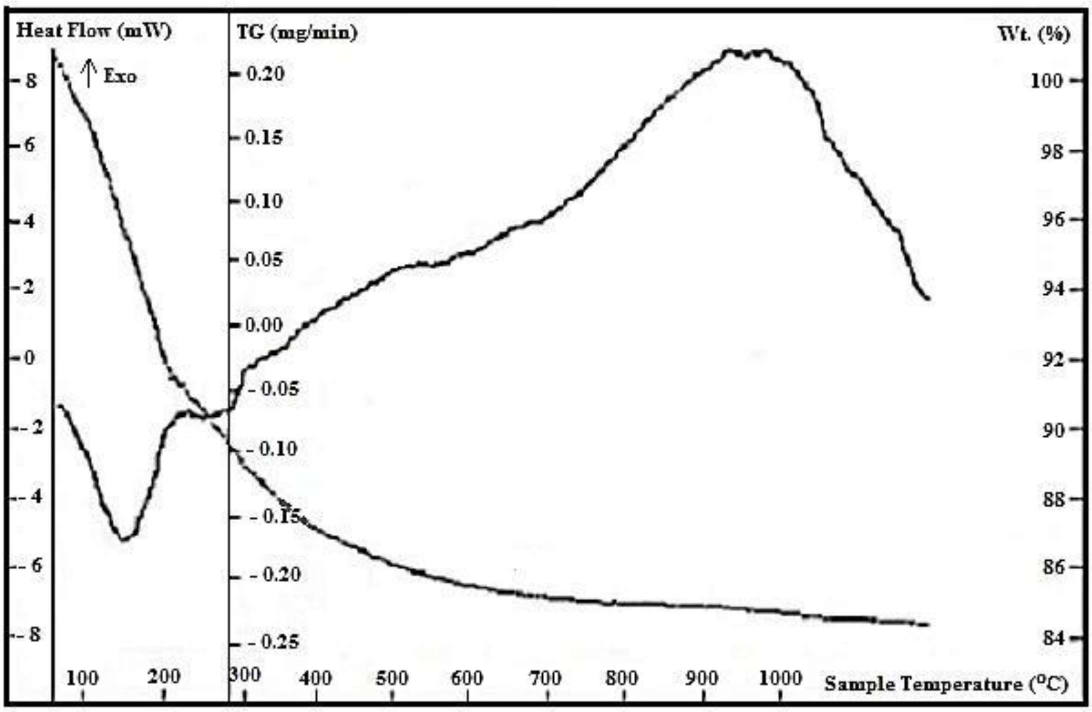


Figure 8.4 TG/ DTA Curves of Test Sample.

8.1.4 Electrokinetic Properties of Zeolite

It was found that; zeolite has negative surface charge at all pH values (Figure 8.5). Zeta potential of it is about -26.50 mV in suspension of neutral pH. The negative charge might be due to substitutions of Al^{3+} some of Si^{4+} within the lattice. In addition, formation of silanol groups the (–SiOH) is another source of negative charge on the surface silanol group dissociates as follow;

$$\sim SiOH \Longleftrightarrow \sim SiO^{-} + H^{+}$$

The negative charge of zeolite surface increased with increasing the pH of the suspension. At pH 12, zeta potential increased to about -35 mV. Due to the H^+ adsorption on the negative charge centers, decreasing the suspension pH lead to decrease of the negative potential. At around pH 2, the zeta potential is about -18 mV; this shows that the clinoptilolite surface maintains its negative character even in very acidic conditions.

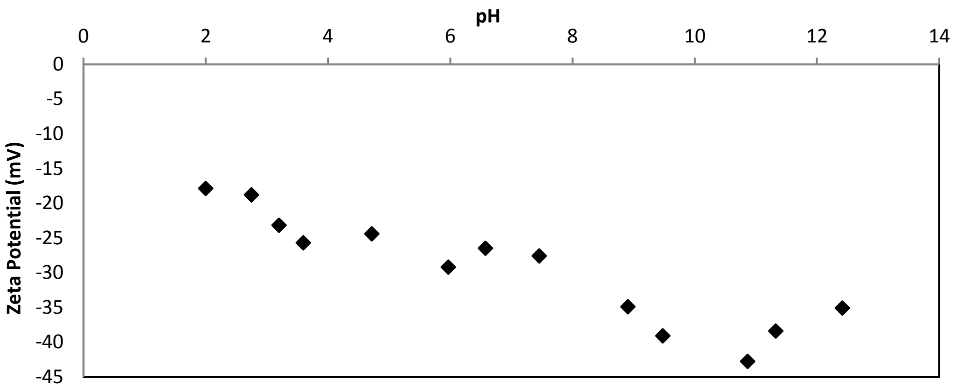


Figure 8.5 Zeta Potential of Zeolite with Respect to pH (App. Table A.1)

8.2 Activation of Zeolite Structure

HCl (0.1 M, 1 M, 5M, 12 M), H_2SO_4 (0.1 M, 1 M), and H_3PO_4 (0.1 M) were used to dissolve amorphous species that may block the channels of zeolite. After treatment with acids, possible changes in chemical composition of zeolite were detected by using XRD and XRF analysis. XRD traces of acid-treated samples are shown in Figure 8.6, 8.7, and their elemental compositions are given in Table 8.1.

It is known that ion exchange is governed by Al^{3+} ions so decreasing of Al_2O_3 amount can cause decreasing ion exchange capacity of zeolite. It is important to improve the ion exchange capacity of zeolite for modification procedure. From the XRF results it can be seen that activation of zeolite with acids decreases the total cation exchange capacity (TCEC) and increase the Si/Al ratio of zeolite. Comparison of results obtained from XRF showed that, activation of zeolite with moderately strong acid (H_3PO_4) did not remove the impurities compared with others and decrease the Si/Al ratio due to unknown mechanism. Therefore, zeolite structure was decided to activate with strong acids (HCl, H_2SO_4). It can be observed from XRF results that, activation of zeolite with HCl can be used for removing impurities from the zeolite structure better than H_2SO_4. The TCEC of activated zeolite with 0.1 M HCl was found as the maximum among the others.

From the XRD patterns of activated zeolite, it can be seen that the intensities of zeolite peaks are decreasing with increasing acid molarity which means that zeolite structure collapsed. So, activation of zeolite structure with 0.1 M HCl was chosen as the best in the activation of it.

Amount of SiO_2 after treatment with HCl of greater than 0.1 M and with H_2SO_4 of all concentration was found to be greater than that of natural zeolite. The reason for this deviation is not known. It might be due to the concentration precipitation which appears as SiO_2.

Table 8.1 Chemical Compositions of Zeolites After Acid Treatment

Oxides	**Natural Zeolite**	**HCl 0,1 M**	**HCl 1 M**	**HCl 5 M**	**HCl 12 M**	**H_2SO_4 0,1M**	**H_2SO_4 1 M**
	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %
SiO_2	75,68	75,65	78,75	81,81	84,74	76,29	78,86
Al_2O_3	14,23	14,22	12,91	11,64	10,21	14,32	12,60
Na_2O	0,68	0,35	0,11	0,08	0,19	0,22	0,21
K_2O	2,20	2,54	2,18	1,40	0,88	2,30	2,29
CaO	3,56	3,54	2,57	1,98	1,54	3,27	2,78
MgO	1,60	1,55	1,28	1,14	0,94	1,45	1,18
Fe_2O_3	1,70	1,44	1,41	1,13	0,78	1,39	1,35
TCEC	2,75	2,69	2,05	1,6	1,26	2,45	2,14
Si/Al	4,52	4,52	5,18	5,97	7,05	4,55	5,32

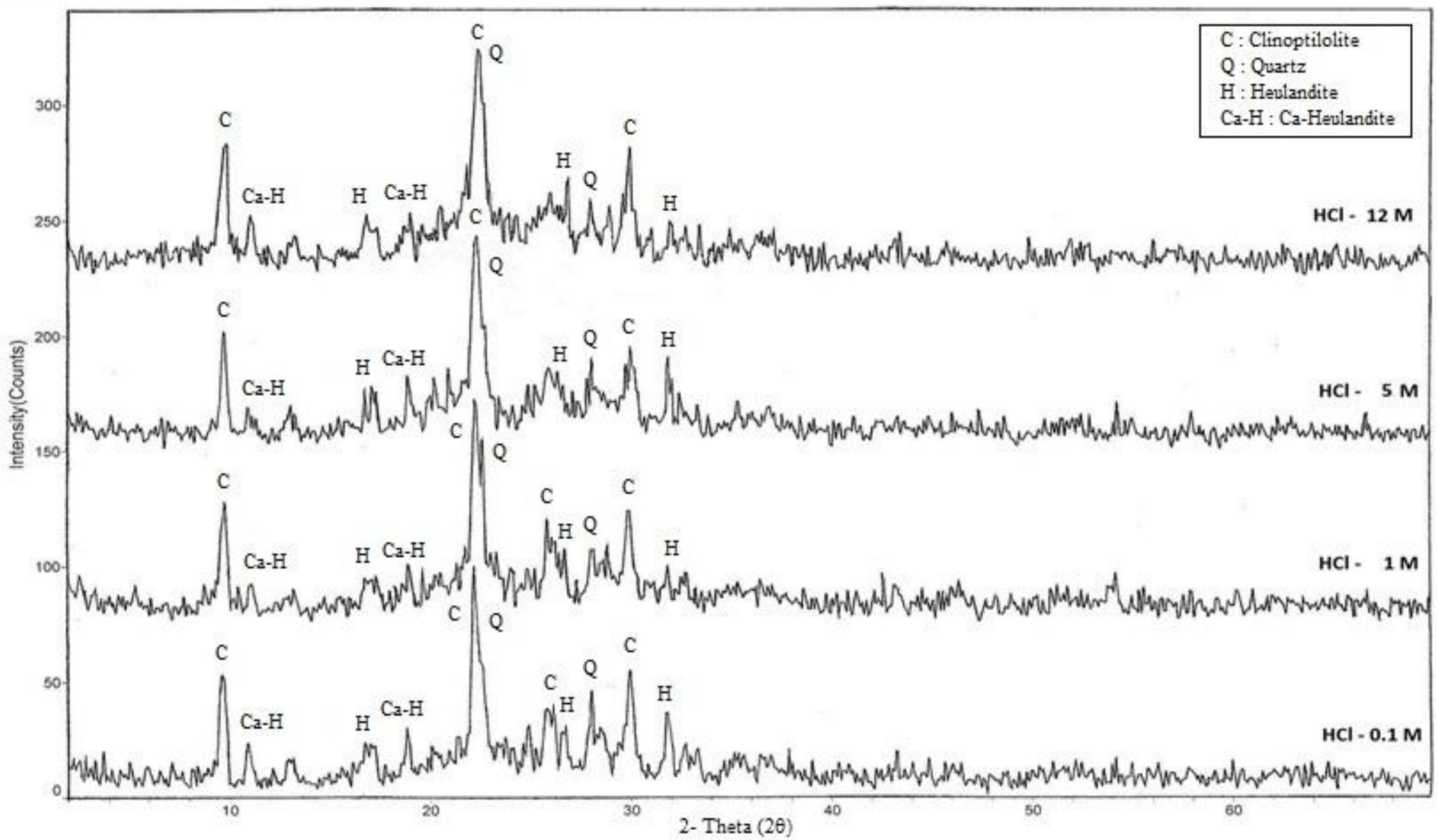


Figure 8.6 XRD Pattern of Zeolite Activated with HCl

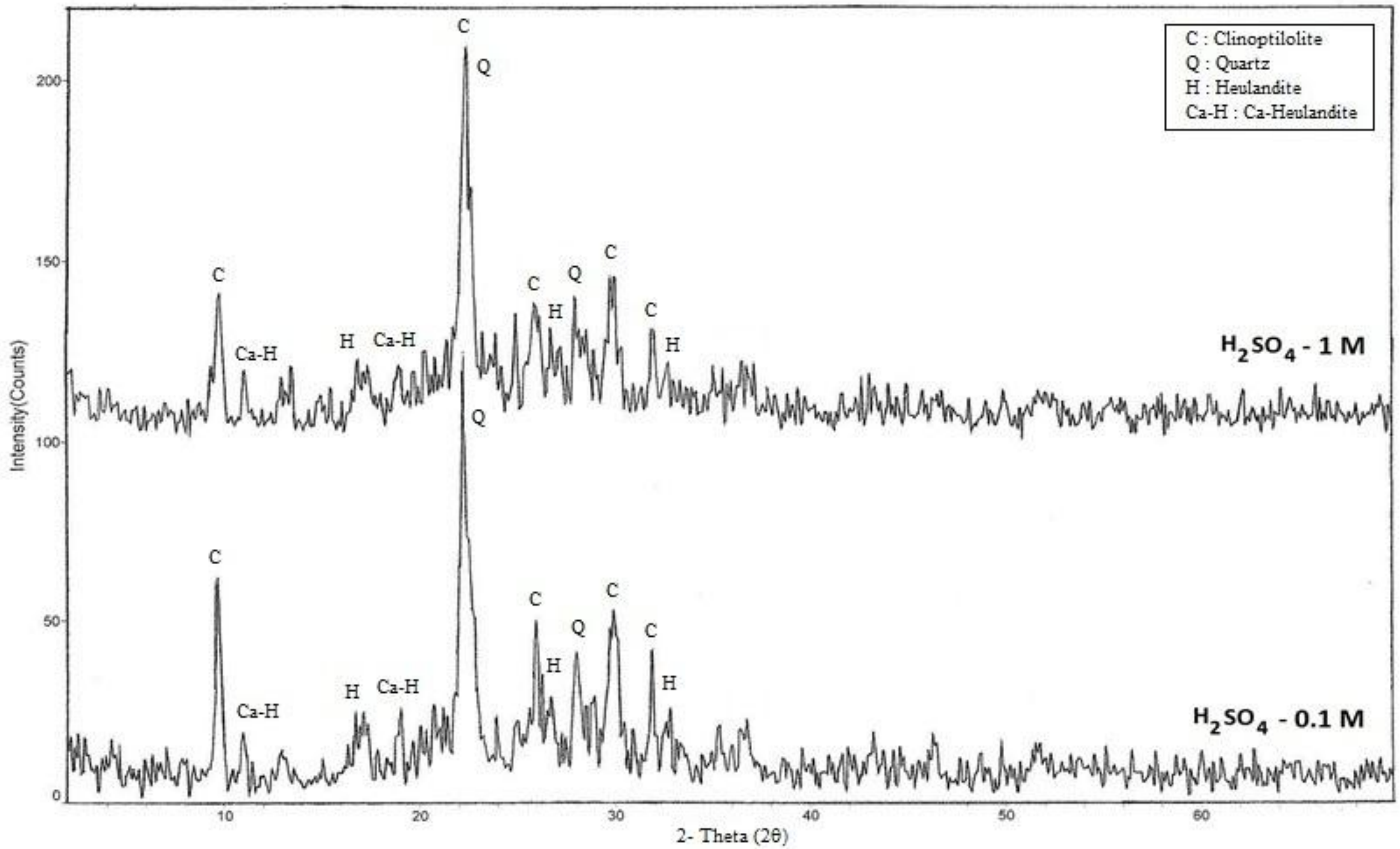


Figure 8.7 XRD Pattern of Zeolite Activated with H_2SO_4

8.3 Adsorption of Cationic Surfactants on Zeolite

Adsorption studies on zeolite were done by using two cationic surfactants namely hexadecyltrimethyl ammonium bromide (HTAB) and dodecyltrimethyl ammonium bromide (DTAB). The effects of contact time, initial concentration of cationic surfactant, and temperature on surfactant adsorption were investigated.

Data obtained in studies was used to calculate the equilibrium quantity of surfactant adsorbed (q_e) by using the following equation;

$$q_e = \frac{(C_e - C_0).V}{W} \tag{14}$$

Where q_e is adsorption capacity of zeolite (mol/g), V is the sample volume (L), C_0 is the initial concentration of surfactant (mol/L), C_e is the equilibrium concentration of surfactant (mol/L), and W is the dry weight of zeolite (g).

8.3.1 Effect of Time

The adsorption of cationic surfactants on zeolite were investigated as a function of time keeping the concentration of cationic surfactants and amount of solid at $1x10^{-2}$ M and 5 g respectively. As shown in Figure 8.8, equilibrium was reached after 1 hour with $1,9x10^{-4}$ mol/g for HTAB, and after 2 hours with $9,96x10^{-5}$ mol/g for DTAB.

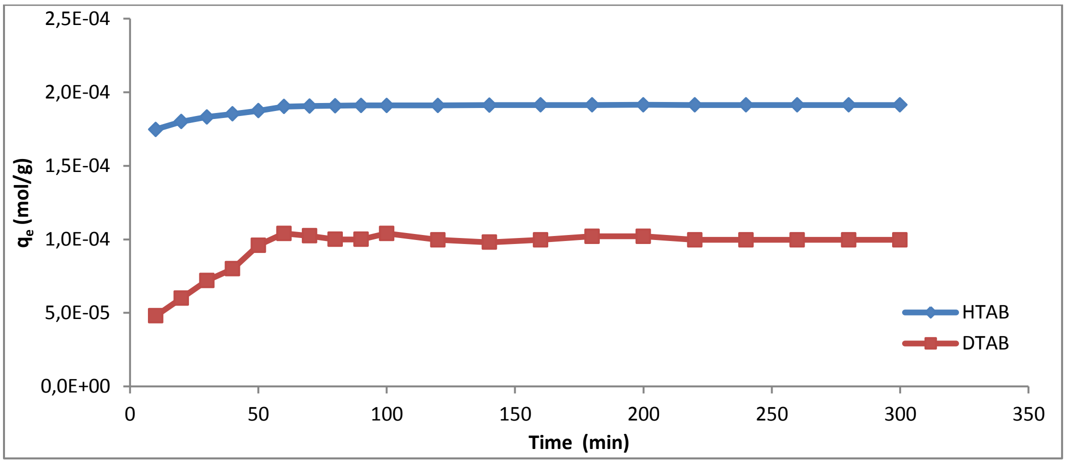


Figure 8.8 Effect of Contact Time on Adsorption of HTAB and DTAB on Zeolite (App. Table B.1, B.2)

8.3.2 Effect of Initial Concentrations of Cationic Surfactants

To investigate the effect of initial cationic surfactant concentration, experiments were carried out by varying initial surfactant concentrations in the range $1x10^{-3}$ - $4x10^{-2}$ mol/L. As shown in Figure 8.9, adsorption capacity of zeolite was reached $2x10^{-4}$ mol/g at $5x10^{-3}$ mol/L equilibrium concentration of HTAB, and $1x10^{-4}$ mol/g at $1.44x10^{-3}$ mol/L equilibrium concentration of DTAB.

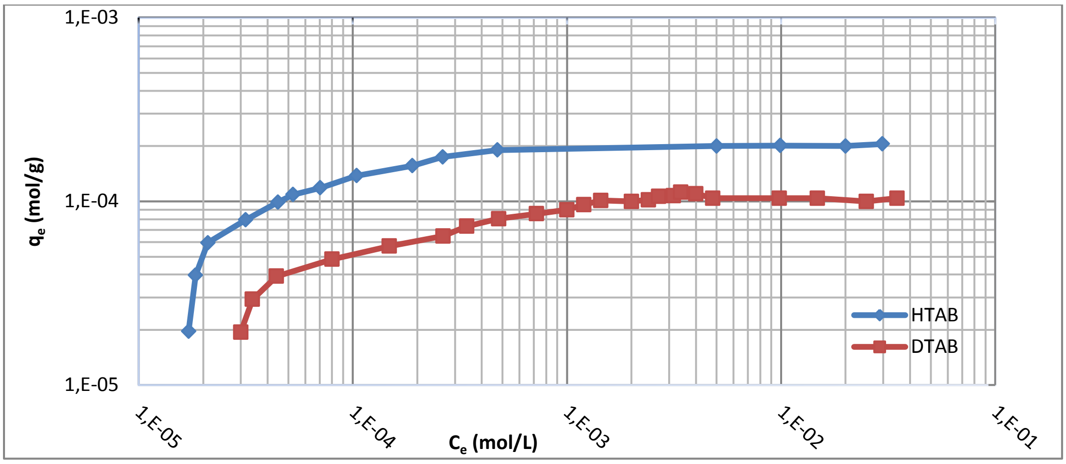


Figure 8.9 Effect of Initial Concentration of Cationic Surfactants on Adsorption (App. Table B.5, B.8)

8.3.3 Electro-kinetic Properties of Organo-Zeolites

Organic cations of surfactants have large polar group ($R (CH_3)_3N^+$, R: $CH_3 (CH_2)_{15}$) and cannot enter into the zeolite channels. They can exchange the surface charge of zeolite surface with their cations. As it is inferred from the zeta potential curve of zeolite (Figure 8.10), up to a certain equilibrium concentration, zeta potential value of zeolite remain almost constant at -34 mV. This means that ion-exchange occurs in an equivalent amount of cations between the zeolite surface and organic cations in the suspension in order to maintain total electroneutrality.

Ion exchange continues until the equilibrium concentrations of $3x10^{-5}$ mol/L for HTAB and $2x10^{-4}$ mol/L for DTAB. After these points, absolute value of zeta potential is decreasing resulting from hydrophobic interaction between particles (Ersoy and Çelik, 2003). Zero point of charge of zeolite was reached at equilibrium concentrations of $5x10^{-5}$ mol/L for HTAB and $6x10^{-3}$ mol/L for DTAB.

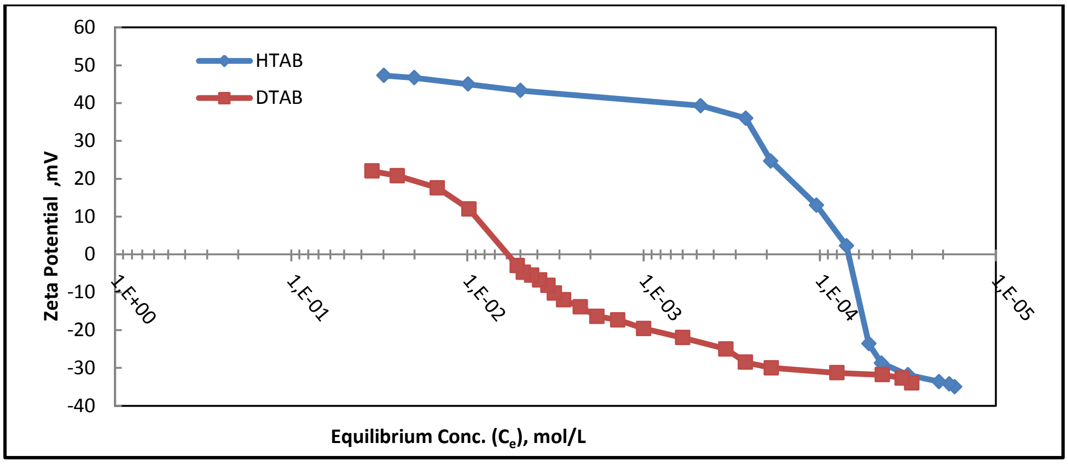


Figure 8.10 Effect of Cationic Surfactants Concentration on Zeta Potential of Zeolite (App. Table B.3, B.4)

As it is seen in Figure 8.11, organic cations of surfactant are adsorbed on zeolite surface by ion exchange mechanism. This mechanism is limited by the cation exchange capacity of the zeolite. The amount of HTAB adsorption through the ion exchange mechanism is greater than those of DTAB. This indicates that the HTAB which has the longer hydrocarbon chain is more conducive to ion exchange. Because, cationic surfactant solubility in water decreases with increasing hydrocarbon chain length (Chen et. al., 1998).

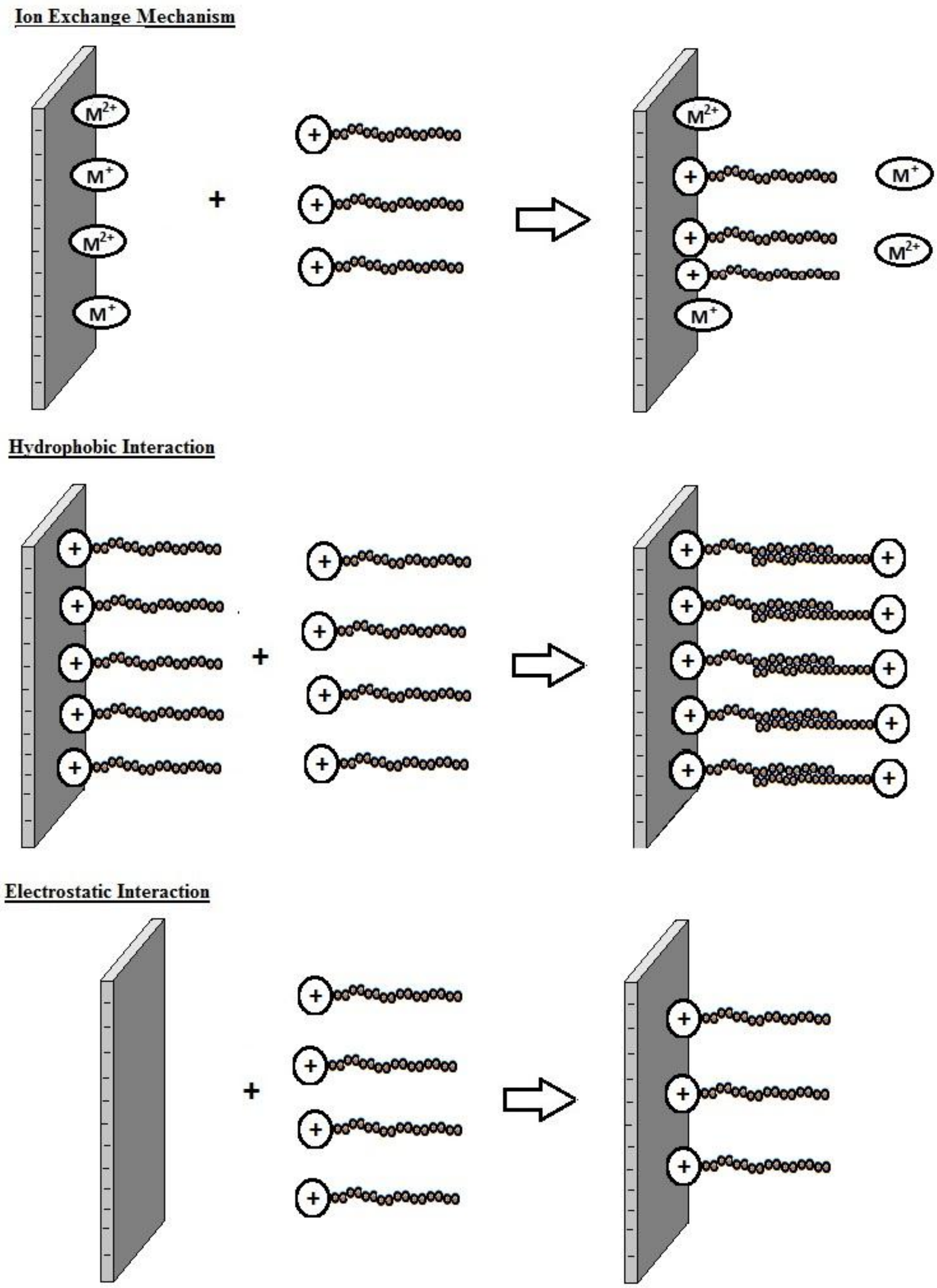


Figure 8.11 Adsorption Mechanisms of Cationic Surfactants on Zeolite (M^{2+}: Divalent cation, M^{+}: Monovalent cation)

8.3.4 Effect of Temperature on Cationic Surfactant Adsorption

To investigate variations in surfactant adsorption with equilibrium concentration, experiments were carried out by varying initial surfactant concentrations at three different temperatures (25°C, 35°C, and 55°C).

Adsorption studies of HTAB were performed by initial concentration between 1 $x10^{-3}$ - 10 $x10^{-3}$ mol/L for an hour. As seen from the Figure 8.12, adsorption capacity of zeolite is decreased with increasing temperature, indicating favorable adsorption process at lower temperatures.

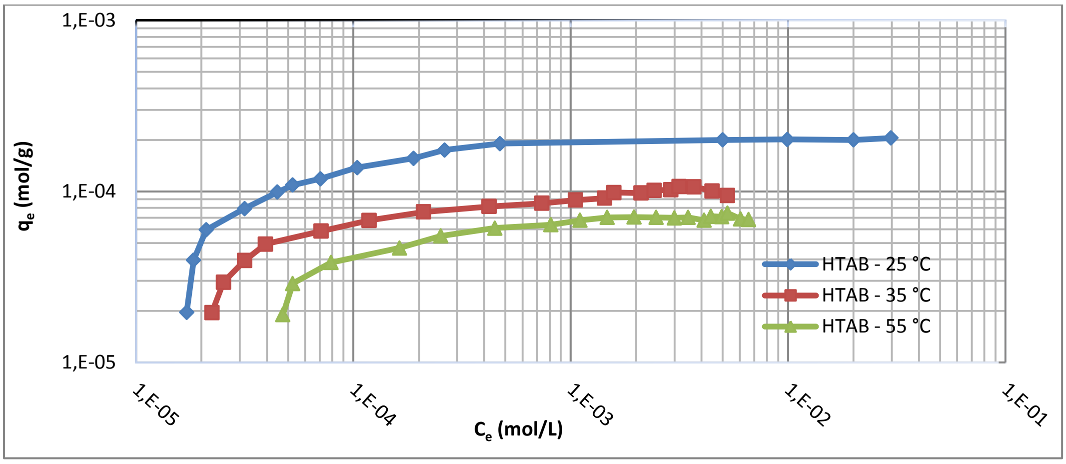


Figure 8.12 Effect of Temperature on Adsorption of HTAB on Zeolite (App. Table B.5, B.6, B.7)

Adsorption studies of DTAB were performed by initial concentration between 1-40 $x10^{-3}$ mol/L for 2 hours. As seen from the Figure 8.13, adsorption capacity of zeolite is increased with temperature, indicating favorable adsorption process at higher temperature.

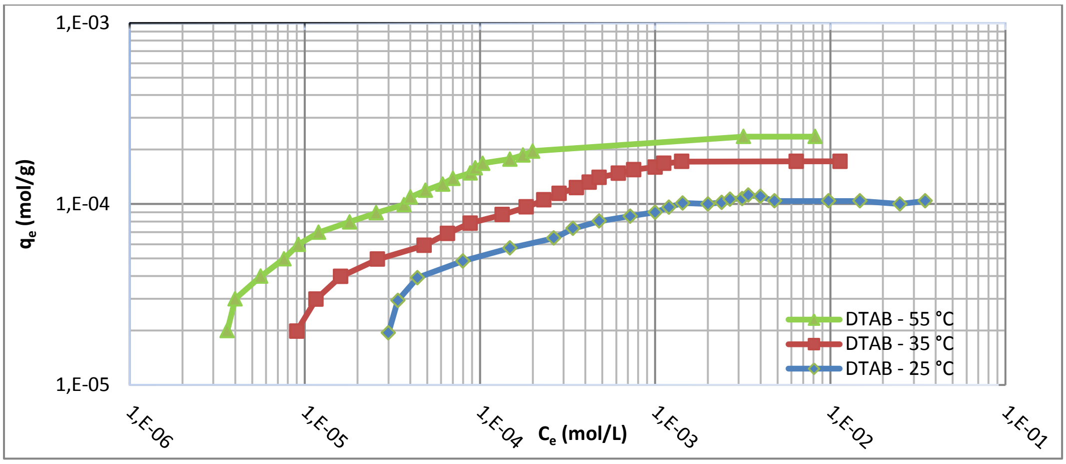


Figure 8.13 Effect of Temperature on Adsorption of DTAB on Zeolite (App. Table B.8, B.9, B.10)

8.3.5 FTIR Analyses of Organo-zeolite

FTIR spectra of natural zeolite and organo-zeolites are shown in Figure 8.14. There are two groups of vibration in all zeolites; internal vibrations of Si-O and vibration of external linkages between tetrahedra, due to topology (see Chapter 3.6) and the mode of structure arrangement (Garza et.al., 2000). FTIR band connected with the internal Si-O (Si) and Si-O (Al) vibrations in tetrahedra or alumino- and silico-oxygen bridges lies in the range of 900-1200 cm^{-1}. The bands due to the presence of zeolite water lie in the range of 1600-3700 cm^{-1}. The bands located at 3517.80 cm^{-1}, 3412.26 cm^{-1}, 3380.54 cm^{-1}, 3315.71 cm^{-1} are attributed to hydrogen bonds participating in adsorbed water molecules.

In FTIR spectra of organo-zeolites, two additional bands were observed; one at 2925.18 and the other at 2853.1 cm^{-1}. These are assigned to the asymmetric and symetric stretching vibrations of C-CH_2 of the alkyl chain, respectively.

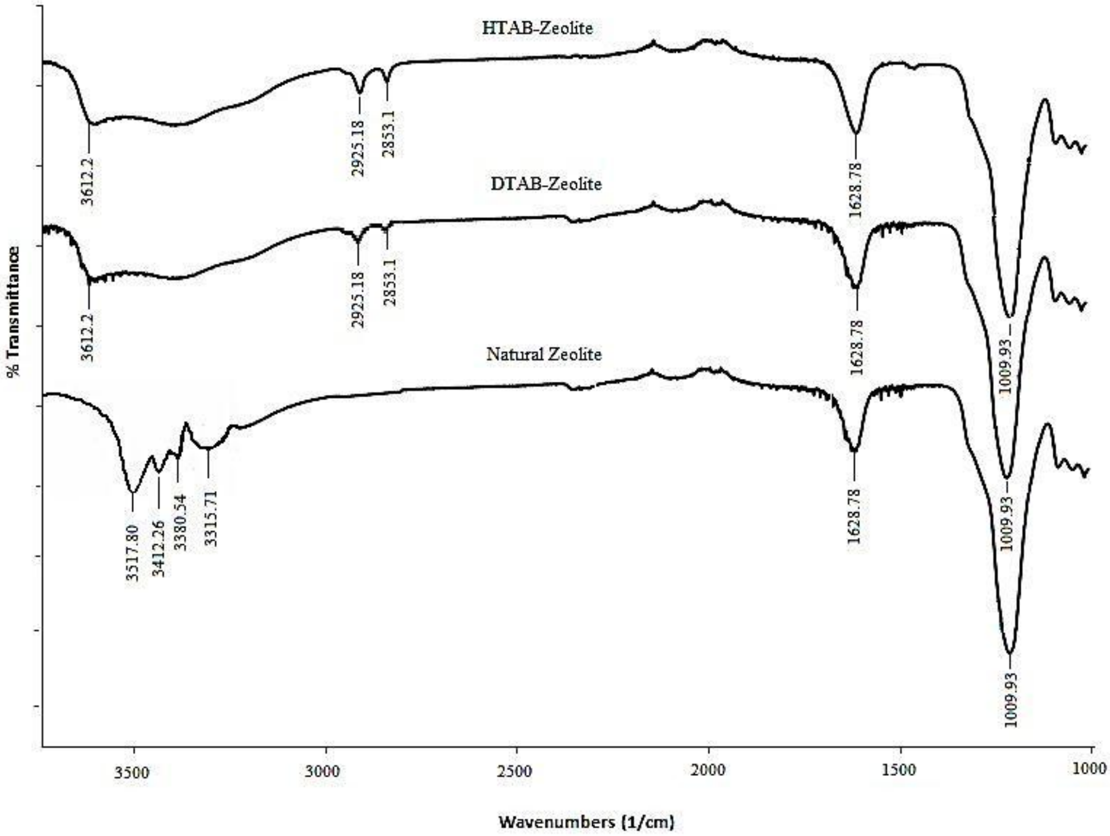


Figure 8.14 FTIR Spectrum of Organo-Zeolite and Natural Zeolite

8.3.6 Effect of Acid Activation of Zeolite on Cationic Surfactant Adsorption

Adsorption of cationic surfactant on acid activated zeolite was performed by varying initial surfactant concentrations in the range $1x10^{-3} – 1.5x10^{-2}$ mol/L.

As can be seen in Figure 8.15, adsorption capacity of acid activated zeolite is lower than that of natural zeolite. This decreasing in adsorption capacity may show that Al^{3+} was removed from the zeolite structure. Adsorption studies which were performed by natural zeolites showed that the main mechanism is the ion exchange mechanism. Therefore, reduction in the amount of aluminum causing a decrease in adsorption capacity of the acid activated zeolite.

Adsorption capacity of activated zeolite was reached 1.5 $x10^{-4}$ mol/g at $4.95x10^{-4}$ mol/L equilibrium concentration of HTAB, and $5.6x10^{-5}$ mol/g at 7.2 $x10^{-3}$ mol/L equilibrium concentration of DTAB.

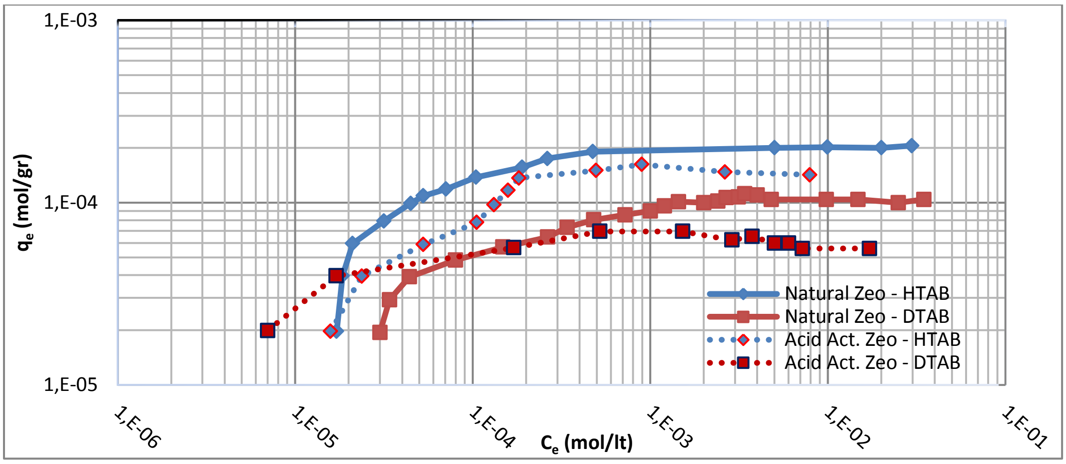


Figure 8.15 Effect of Acid Activation of Zeolite on Adsorption of HTAB and DTAB (App. Table B.5, B.8, B.11, B.13)

8.3.7 Effect of Thermal Activation of Zeolite on Adsorption

Adsorption studies with thermally activated zeolites were carried out keeping the concentration of cationic surfactants and solid amount constant at $1x10^{-3}$ M and 5 g respectively. Thermal activation temperature was varied between 100°C and 500°C considering the results of TG/DTA. According to the results from the adsorption studies, 300°C was chosen as the optimum thermal activation temperature.

The effect of thermal activation on adsorption of cationic surfactants on zeolite is shown in Figure 8.16. Adsorption capacity was reached to $1.9\ x10^{-4}$ mol/g at $1.05x10^{-3}$ mol/L equilibrium concentration of HTAB, and $7x10^{-5}$ mol/g at $4.5\ x10^{-3}$ mol/L equilibrium concentration of DTAB. It can be observed that adsorption capacity of thermally activated zeolite coated with cationic surfactant is lower than that of natural zeolite coated with cationic surfactant. This situation may be explained by migration of exchangeable cations to fixed places that are more stable but more difficult to undergo ion exchange with removing the zeolitic water from the structure.

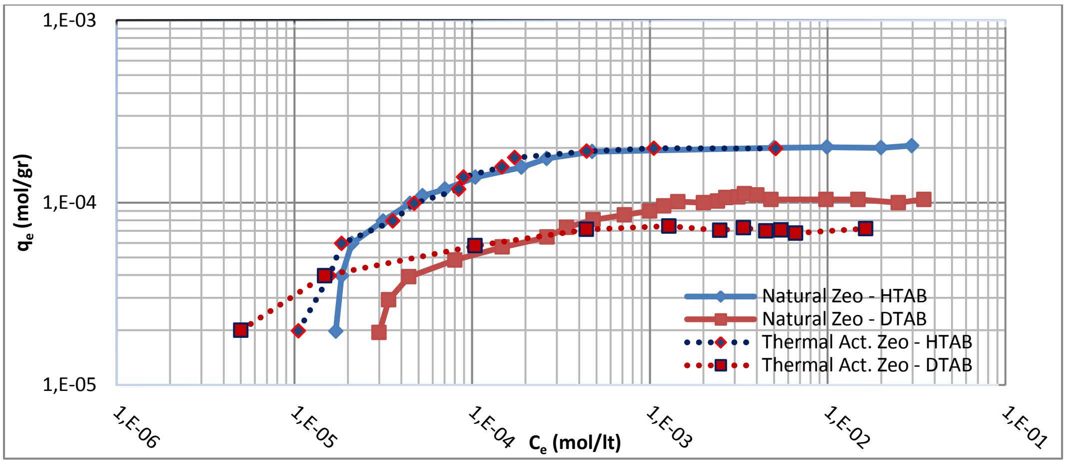


Figure 8.16 Effect of Thermal Activation of Zeolite on Adsorption of HTAB and DTAB (App. Table B.5, B.8, B.12, B.14)

8.3.8 Adsorption Isotherms

To describe the sorption characteristic of zeolite, two adsorption models (Langmuir and Freundlich isotherm model) were applied.

According to previous results obtained by investigation of changes in zeta potential of zeolite with cationic surfactant, the main mechanisms were assumed as ion exchange, hydrophobic and electrostatic interactions. In ion exchange mechanism, adsorption occurs on zeolite surface as monolayer which is described by Langmuir isotherm; and in hydrophobic and electrostatic interaction mechanisms, adsorption occurs on zeolite surface as multilayer which is described by Freundlich isotherm.

Figure 8.17 present adsorption isotherms of cationic surfactants at different temperatures. Parameters related to each isotherm were determined by using linear regression analysis and the square of the correlation coefficients (R^2) have been calculated. A list of the parameters obtained together with R^2 values is provided in Table 8.2.

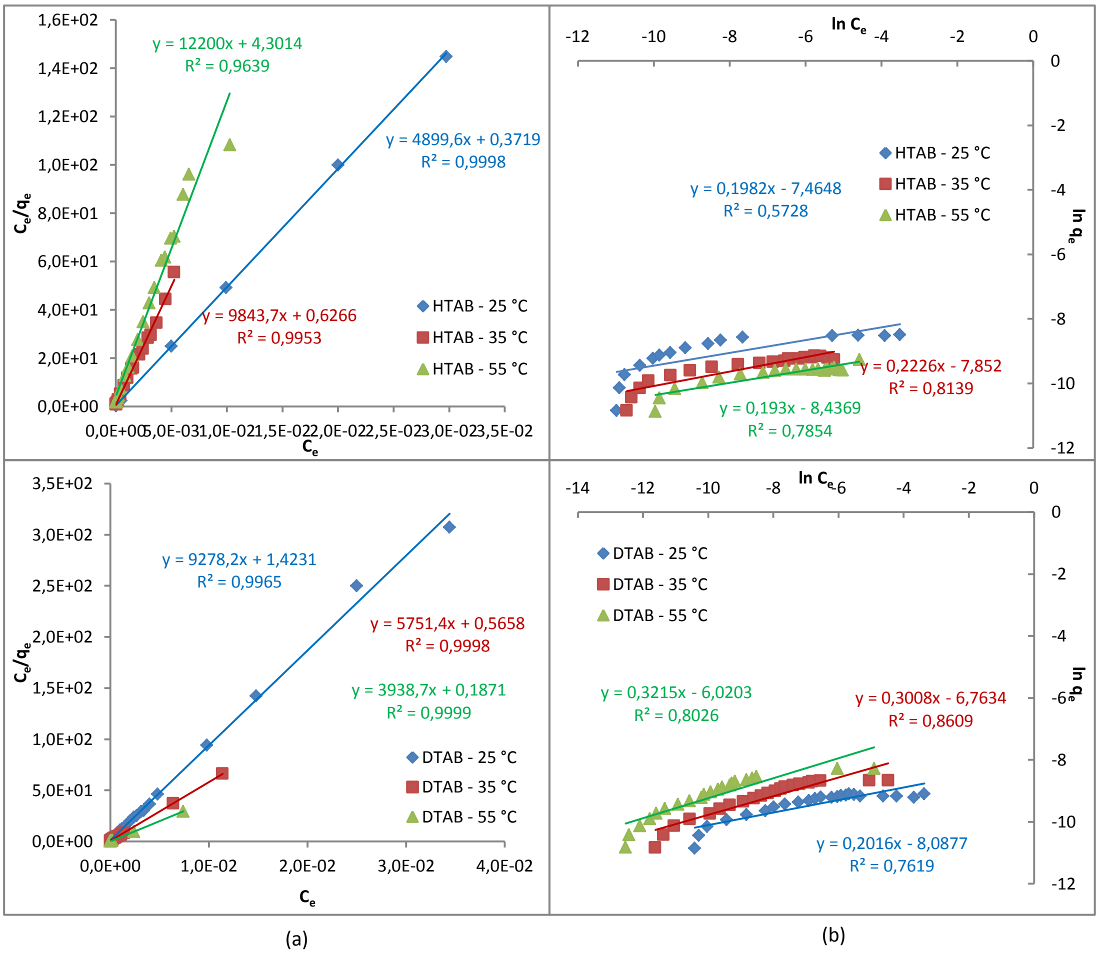


Figure 8.17 Adsorption Isotherms of HTAB and DTAB on Zeolite. (a) Langmuir Isotherm, (b) Freundlich Isotherm (App. Table B.15, B.16, B.17, B.18, B.19, B.20, B.21, B.22, B.23, B.24, B.25, B.26)

It has been found that the best fitted isotherm equation was Langmuir equation (evidenced from the correlation coefficients, >0.990) which is the useful equilibrium model in understanding the type of adsorbent/adsorbate interactions (physical or chemical) involved.

Linear plots of C_e/q_e versus C_e were employed to determine the value of q_{max} (mol/g) and K_L (L/mg). The correlation coefficient of Freundlich isotherm equation (< 0.90) is lower than that obtained for the Langmuir equation. Linear plots of ln q_e versus ln C_e employed to determine value of Freundlich constants (n and K_F).

Table 8.2 Parameters of Adsorption Isotherms of HTAB and DTAB on the Zeolite at Different Temperature

		Langmuir Isotherm			Freundlich Isotherm		
	Temperature (C°)	q_{max} (mol/g)	K_L (L/mol)	R^2	K_f	n	R^2
HTAB-Zeo	25 °C	2.04×10^{-4}	$1.32 \times 10^{+4}$	0.999	5.73×10^{-4}	5.05	0.573
	35 °C	1.02×10^{-4}	$1.57 \times 10^{+4}$	0.995	3.89×10^{-4}	4.50	0.814
	55 °C	8.20×10^{-5}	$2.84 \times 10^{+3}$	0.963	2.17×10^{-4}	5.18	0.785
DTAB-Zeo	25 °C	1.08×10^{-4}	$6.52 \times 10^{+3}$	0.997	3.07×10^{-4}	4.96	0.762
	35 °C	1.74×10^{-4}	$1.02 \times 10^{+4}$	0.999	1.16×10^{-3}	3.33	0.860
	55 °C	2.54×10^{-4}	$2.11 \times 10^{+4}$	0.999	2.43×10^{-3}	3.11	0.802

As it is seen from the Table 8.2, the adsorption amount of HTAB is decreased with increasing temperature from 25° C to 55° C, indicating that the adsorption of HTAB was controlled by an exothermic process. This can be due to a weakening of the attractive forces between HTAB molecules and adsorbent sites at higher temperatures. Unlike adsorption of HTAB, the adsorption amount of DTAB is increasing with increasing temperature from 25° C to 55° C. This indicates that the adsorption of DTAB was controlled by an endothermic process. It is well known that, solubility and mobility of organic compounds increase with increasing temperature. Therefore, increase in the amount of DTAB adsorption is unexpected situation. Attractive forces between the DTAB molecules and adsorbent surface may be broken due to the high temperature. So, DTAB molecules may be deposited on the zeolite surface.

8.3.9 Kinetics Parameters of Adsorption

A study of adsorption kinetics is desirable as it provides information about the mechanism of adsorption. Kinetic studies were performed keeping the concentration of cationic surfactants and solid amount fixed at 1×10^{-2} M and 5 g respectively at 25°C.

The modeling of the kinetics of adsorption of cationic surfactants on zeolite was investigated by two common models, namely, Lagergren pseudo-first-order and pseudo-second-order model.

Lagergren pseudo-first-order kinetic model is expressed as:

$$\log (q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \quad (15)$$

Where, q_e and q_t arethe amounts of surfactant adsorbed at equilibrium (mol/g), and at time t (min), respectively. The equilibrium adsorption capacity (q_e), and the first order rate constant (k_1) were calculated from the slope and y-intercept of the linear plot of log (q_e-q_t) versus time (Figure 8.18(a)).

Pseudo-second-order kinetic model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (16)$$

Where, q_e and q_t are the amounts of surfactant adsorbed at equilibrium (mol/g), and at time t (min), respectively. The equilibrium adsorption capacity (q_e), and the second order rate constant (k_2) were calculated from the slope and y-intercept of the linear plot of t/q_t versus time (Figure 8.18(b)).

The constants of pseudo-first-order kinetic model (k_1 and q_e) and pseudo-second-order kinetic model (k_2 and q_e) are presented in Table 8.3 along with the corresponding correlation coefficients.

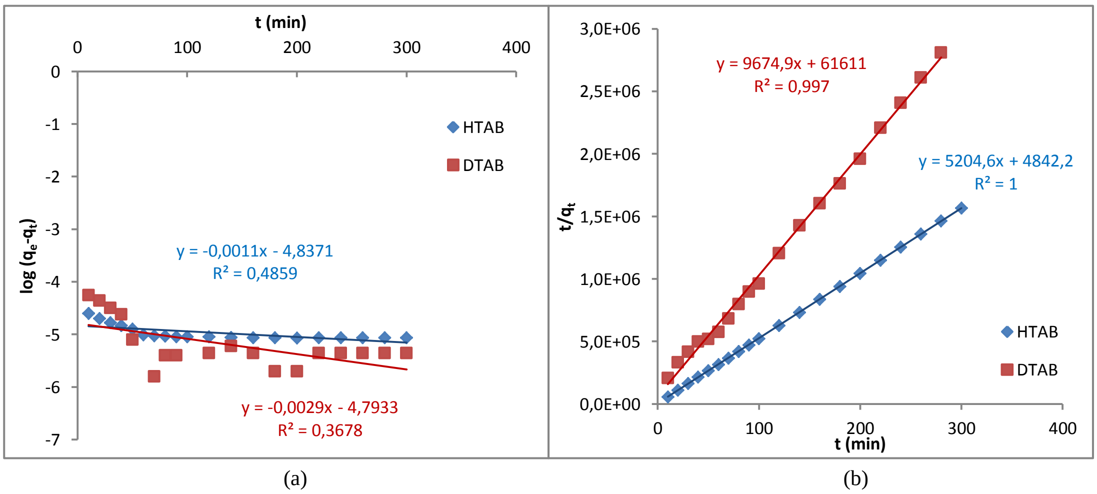


Figure 8.18 Comparison of Kinetic Models of Cationic Surfactants on Zeolite. (a) First Order Kinetics, (b) Second Order Kinetics (App. Table B.27, B.28, B.29, B.30)

As it can be seen from the Table 8.3, the correlation coefficient (R^2) for the pseudo-second-order kinetic model has high value (> 0.99), and its calculated equilibrium adsorption capacity ($q_{e,cal}$) is consistent with experimental data. These facts suggest that pseudo-second-order adsorption mechanism is predominant.

Table 8.3 Parameters of Kinetic Models of Cationic Surfactants on Zeolite

	Pseudo First Order			**Pseudo Second Order**		
	k_1	$q_{e,cal}$	R^2	k_2	$q_{e,cal}$	R^2
HTAB	2.30E-03	1.4555E-05	0.4859	5.59E+03	1.92E-04	1
DTAB	4.61E-03	1.6106E-05	0.3678	1.52E+03	1.03E-04	0.997

8.3.10 Thermodynamics Parameters of Adsorption

To estimate the effect of temperature on the adsorption of cationic surfactants onto zeolite, the free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were calculated using Eq (17), (18), and (19).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{17}$$

$$\Delta G^\circ = -RT(\ln K) \tag{18}$$

Taking advantages of Eqs. (17) and (18), the van’t Hoff equation can be written as

$$\ln K = \frac{\Delta S^\circ}{T} + \frac{\Delta H^\circ}{RT} \tag{19}$$

where, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K°), K is the adsorption equilibrium constant.

A plot of ln K against the reciprocal of absolute temperature, 1/T, give straight line as shown in Figure 8.19; enthalpy change (ΔH°) entropy change (ΔS°) were calculated from the slope and y-intercept of plot as documented in Table 8.4.

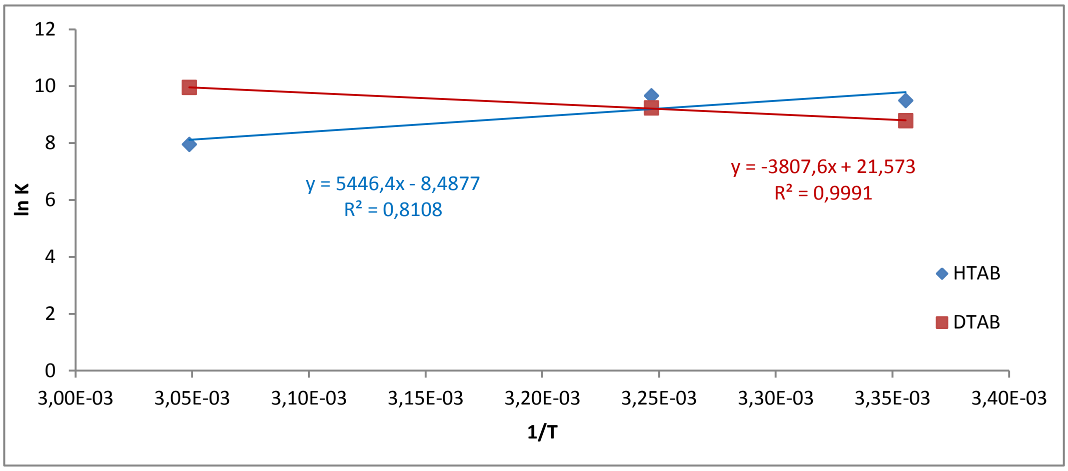


Figure 8.19 Van't Hoff Plot for the Adsorption of Surfactants on Zeolite

The negative values of ΔH° and ΔG° for HTAB exhibit the exothermic and spontaneous nature of the sorption process at all temperatures respectively.

The positive value of ΔH° and the negative value of ΔG° for DTAB exhibit the endothermic and spontaneous nature of the sorption process at all temperatures respectively.

Positive ΔS° approves the increased randomness at the solid-liquid interface during adsorption. The low value of ΔS also indicates that no remarkable changed on entropy occurs.

Table 8.4 Thermodynamic Parameters for Adsorption of Surfactants on Zeolite

	Tem. (K°)	K_L	ln K_L	1/T	ΔH (kJ/mol)	ΔS (kJ/mol)	TΔS (kJ/mol)	ΔG (kJ/mol)
HTAB	298	1.32E+04	9.488	3.36E-03	-45.28	-0.07	-21.03	-24.25
	308	1.57E+04	9.661	3.25E-03			-21.73	-23.54
	328	2.84E+03	7.952	3.05E-03			-23.14	-22.13
DTAB	298	6.52E+03	8.783	3.36E-03	31.61	0.18	53.40	-21.79
	308	1.02E+04	9.230	3.25E-03			55.19	-23.58
	328	2.11E+04	9.957	3.05E-03			58.77	-27.16

8.4 Adsorption of Pesticides on Organo-Zeolite and Activated Carbon

Adsorption of pesticides on organo-zeolites and activated carbon was performed by varying initial pesticides concentrations keeping the amount of pesticide and adsorbent (organo-zeolites and activated carbon) constant at 10 mL and 0.5 gr, respectively. Residual pesticide concentrations in suspensions were measured using Ultraviolet Double-Beam Spectroscopy (UV) at their related wavelength.

Data obtained in batch mode studies was used to calculate the equilibrium pesticide adsorption quantity by using the equation given (Eq. 14).

8.4.1 Effect of Contact Time and Initial Concentration of Pesticide

In order to determine the contact time, adsorption experiments were performed with different initial concentrations of pesticides selected on the basis of their solubility in water. Generally, adsorption capacities of adsorbents (organo-zeolite and activated carbon) are increased with increasing initial concentration of pesticide. Whereas, amount of adsorbed pesticide is decreased with increasing initial concentration of pesticides. Adsorption experiments have shown that adsorption capacity of HTAB-Zeolite is higher than that of DTAB-Zeolite. These differences between the HTAB-Zeolite and DTAB-Zeolite may be due to the selection of the more hydrophobic surface by pesticide.

According to the calculated results, it can be observed that, activated carbon have shown higher adsorption capacity than organo-zeolites. This can be expressed by its well-developed pores which is suitable for adsorption of pesticide.

Initial concentrations of 2,4-D were selected as 250, 350, and 450 mg/L. Adsorption capacities of organo-zeolites and activated carbon are shown in Figure 8.20(a) and amount of adsorbed pesticide at equilibrium concentrations are shown in Figure

8.20(b). The amount of adsorbed pesticide, adsorption capacities of adsorbents and contact time to reach equilibrium concentration are tabulated in Table 8.5.

Table 8.5 The Effect of Initial 2,4-D Concentration on Adsorption

Adsorbent	Initial Concentration of 2,4-D (mg/L)	Equilibrium Time (min)	Adsorption Capacity (mol/g)	Amount of Adsorbed Pesticide (%)
HTAB-Zeo	450	220	2.224×10^{-5}	54.62
	350	200	1.85×10^{-5}	58.42
	250	220	1.574×10^{-5}	69.60
DTAB-Zeo	450	140	8.539×10^{-6}	20.97
	350	140	7.878×10^{-6}	24.88
	250	140	6.098×10^{-6}	26.96
Activated Carbon	450	420	2.238×10^{-5}	54.96
	350	400	2.172×10^{-5}	68.57
	250	320	1.620×10^{-5}	71.64

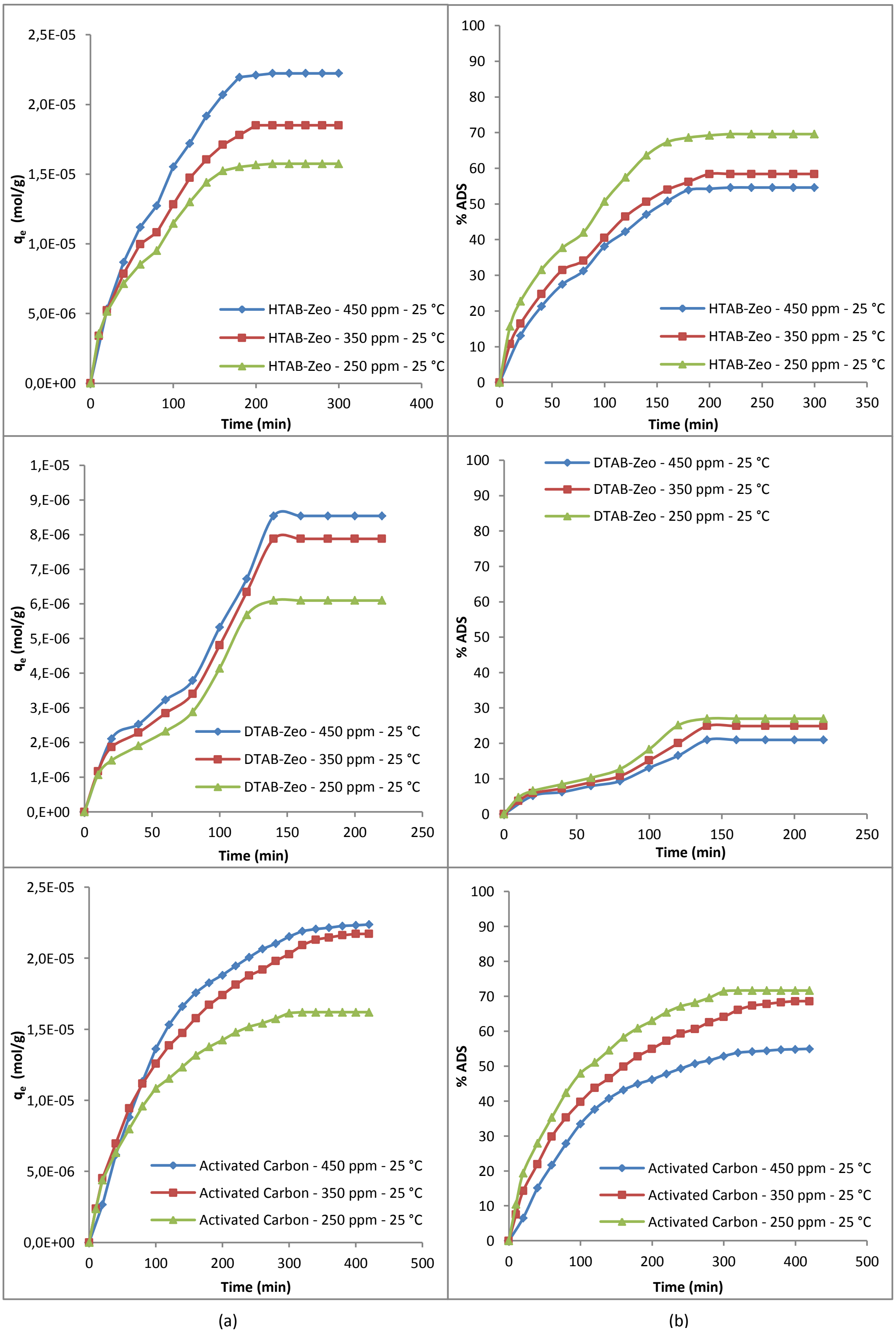


Figure 8.20 Effect of Contact Time and Initial Concentration of 2,4-D on Adsorption (App. Table C.1, C.4, C.7). (a) Adsorption Capacities of Adsorbents (b) Amount of Adsorbed Pesticide on Adsorbents

Initial concentrations of propanil were selected as 60, 80, and 100 mg/L. Adsorption capacities of organo-zeolites and activated carbon are shown in Figure 8.21(a) and amount of adsorbed pesticide at equilibrium concentrations are shown in Figure 8.21(b). The amount of adsorbed pesticide, adsorption capacities of adsorbents and contact time to reach equilibrium concentration are tabulated in Table 8.6.

Table 8.6 The Effect of Initial Propanil Concentration on Adsorption

Adsorbent	Initial Concentration of Propanil (mg/L)	Equilibrium Time (min)	Adsorption Capacity (mol/g)	Amount of Adsorbed Pesticide (%)
HTAB-Zeo	100	160	5.00×10^{-6}	54.59
	80	140	4.516×10^{-6}	61.56
	60	120	3.758×10^{-6}	68.29
DTAB-Zeo	100	180	2.586×10^{-6}	28.20
	80	160	2.365×10^{-6}	32.24
	60	160	1.916×10^{-6}	34.82
Activated Carbon	100	380	5.88×10^{-6}	64.12
	80	380	5.189×10^{-6}	70.72
	60	380	4.00×10^{-6}	72.69

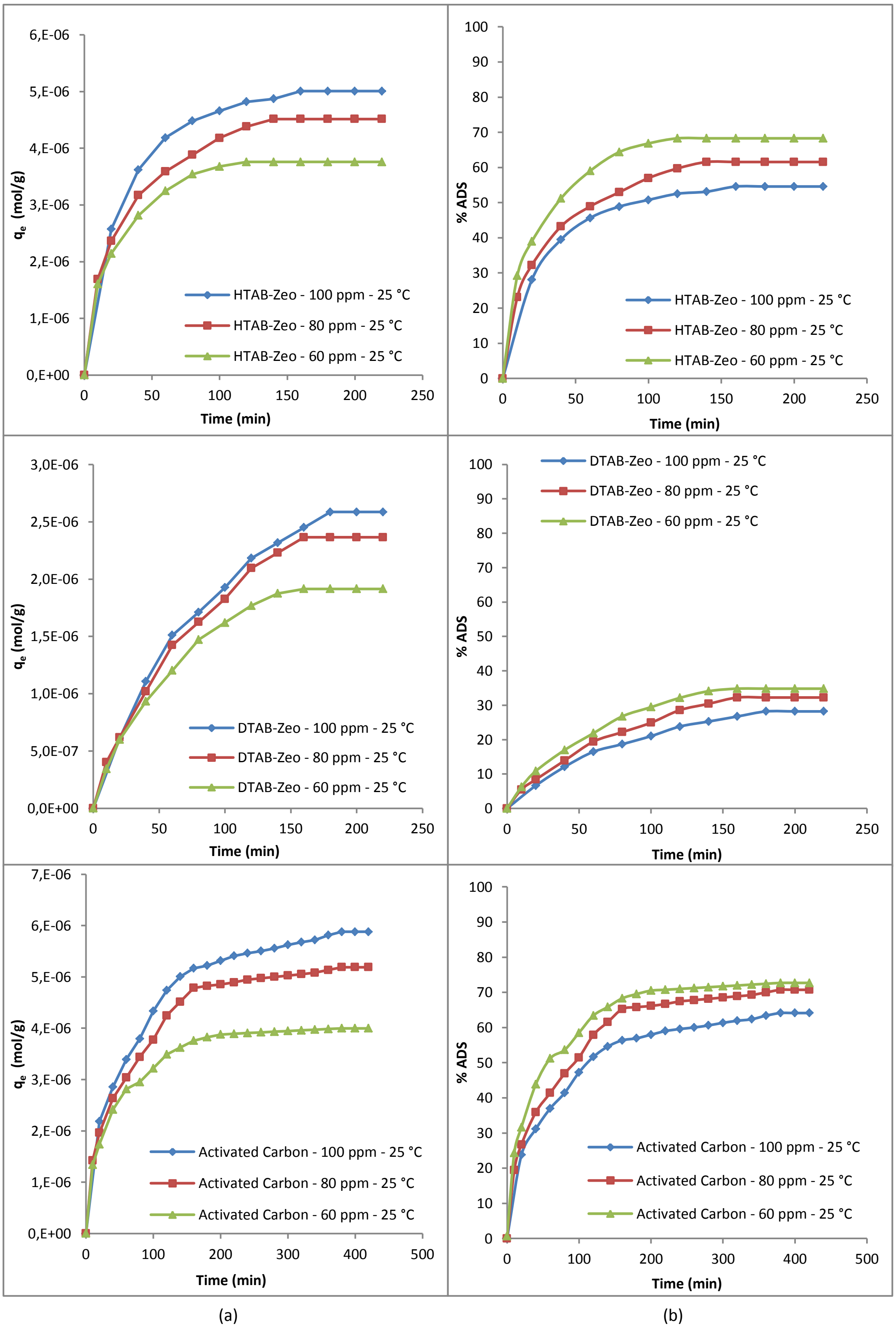


Figure 8.21 Effect of Contact Time and Initial Concentration of Propanil on Adsorption (App. Table C.25, C.28, C.31). (a) Adsorption Capacities of Adsorbents (b) Amount of Adsorbed Pesticide on Adsorbents

Initial concentrations of diazinon were selected as 30, 40, and 50 mg/L. Adsorption capacities of organo-zeolites and activated carbon are shown in Figure 8.22(a) and amount of adsorbed pesticide at equilibrium concentrations are shown in Figure 8.22(b). The amount of adsorbed pesticide, adsorption capacities of adsorbents and contact time to reach equilibrium concentration are tabulated in Table 8.7.

Table 8.7 The Effect of Initial Diazinon Concentration on Adsorption

Adsorbent	Initial Concentration of Diazinon (mg/L)	Equilibrium Time (min)	Adsorption Capacity (mol/g)	Amount of Adsorbed Pesticide (%)
HTAB-Zeo	50	200	2.00×10^{-6}	60.97
	40	180	1.652×10^{-6}	62.86
	30	160	1.244×10^{-6}	63.11
DTAB-Zeo	50	200	1.085×10^{-6}	33.01
	40	200	9.634×10^{-7}	36.65
	30	200	7.618×10^{-7}	38.64
Activated Carbon	50	320	2.271×10^{-6}	69.13
	40	300	1.897×10^{-6}	72.18
	30	300	1.474×10^{-6}	74.76

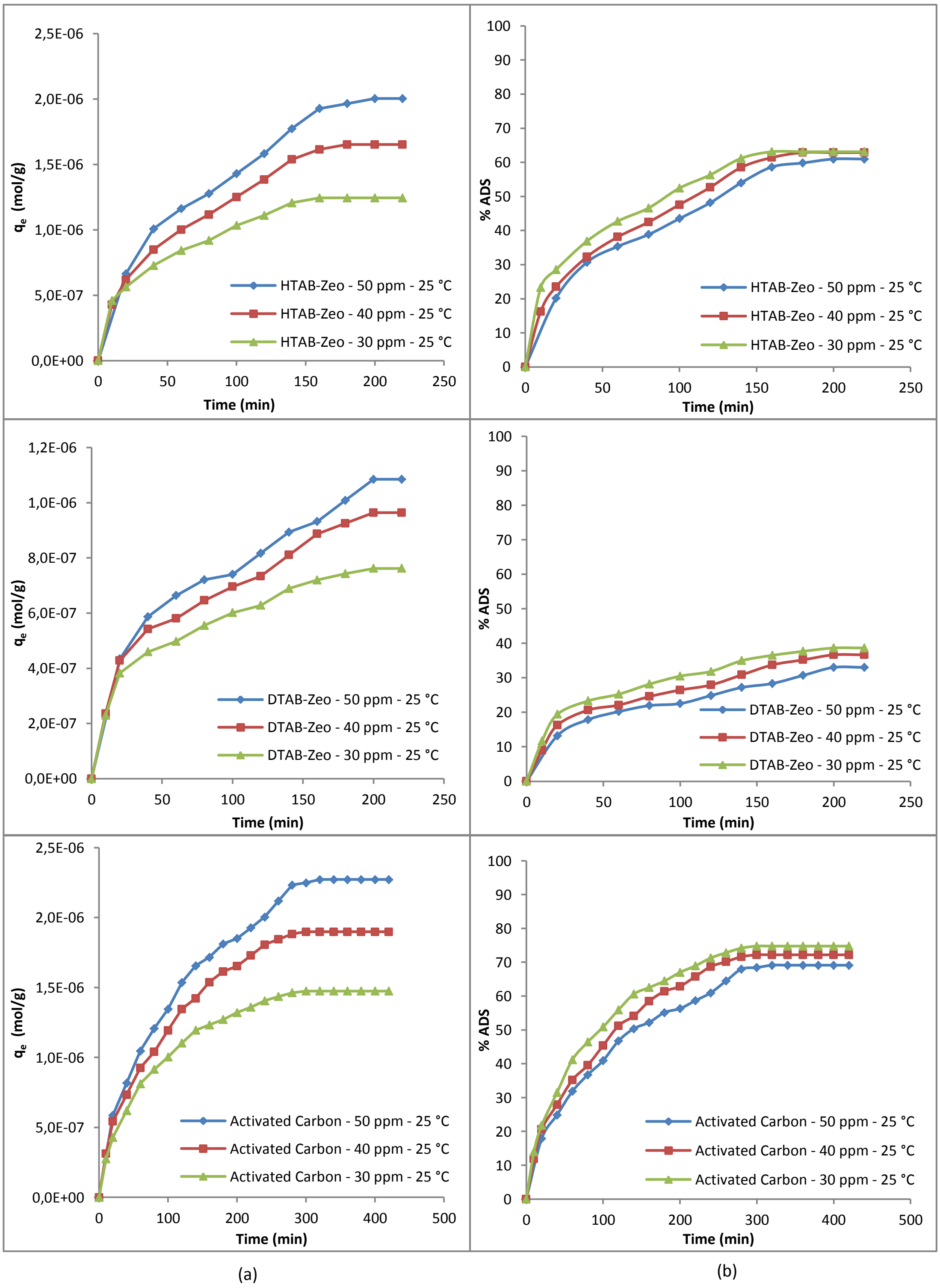


Figure 8.22 Effect of Contact Time and Initial Concentration of Diazinon on Adsorption (App. Table C.49, C.52, C.55). (a) Adsorption Capacities of Adsorbents (b) Amount of Adsorbed Pesticide on Adsorbents

Initial concentrations of fenitrothion were selected as 5, 10, and 20 mg/L. Adsorption capacities of organo-zeolites and activated carbon are shown in Figure 8.23(a) and amount of adsorbed pesticide at equilibrium concentrations are shown in Figure 8.23(b). The amount of adsorbed pesticide, adsorption capacities of adsorbents and contact time to reach equilibrium concentration are tabulated in Table 8.8.

Table 8.8 The Effect of Initial Fenitrothion Concentration on Adsorption

Adsorbent	Initial Concentration of Fenitrothion (mg/L)	Equilibrium Time (min)	Adsorption Capacity (mol/g)	Amount of Adsorbed Pesticide (%)
HTAB-Zeo	20	120	8.916×10^{-7}	61.79
	10	100	5.118×10^{-7}	70.95
	5	100	2.688×10^{-7}	74.53
DTAB-Zeo	20	160	6.331×10^{-7}	43.88
	10	140	3.424×10^{-7}	47.46
	5	100	1.927×10^{-7}	53.43
Activated Carbon	20	300	1.035×10^{-6}	71.74
	10	300	5.405×10^{-7}	74.93
	5	280	2.861×10^{-7}	79.30

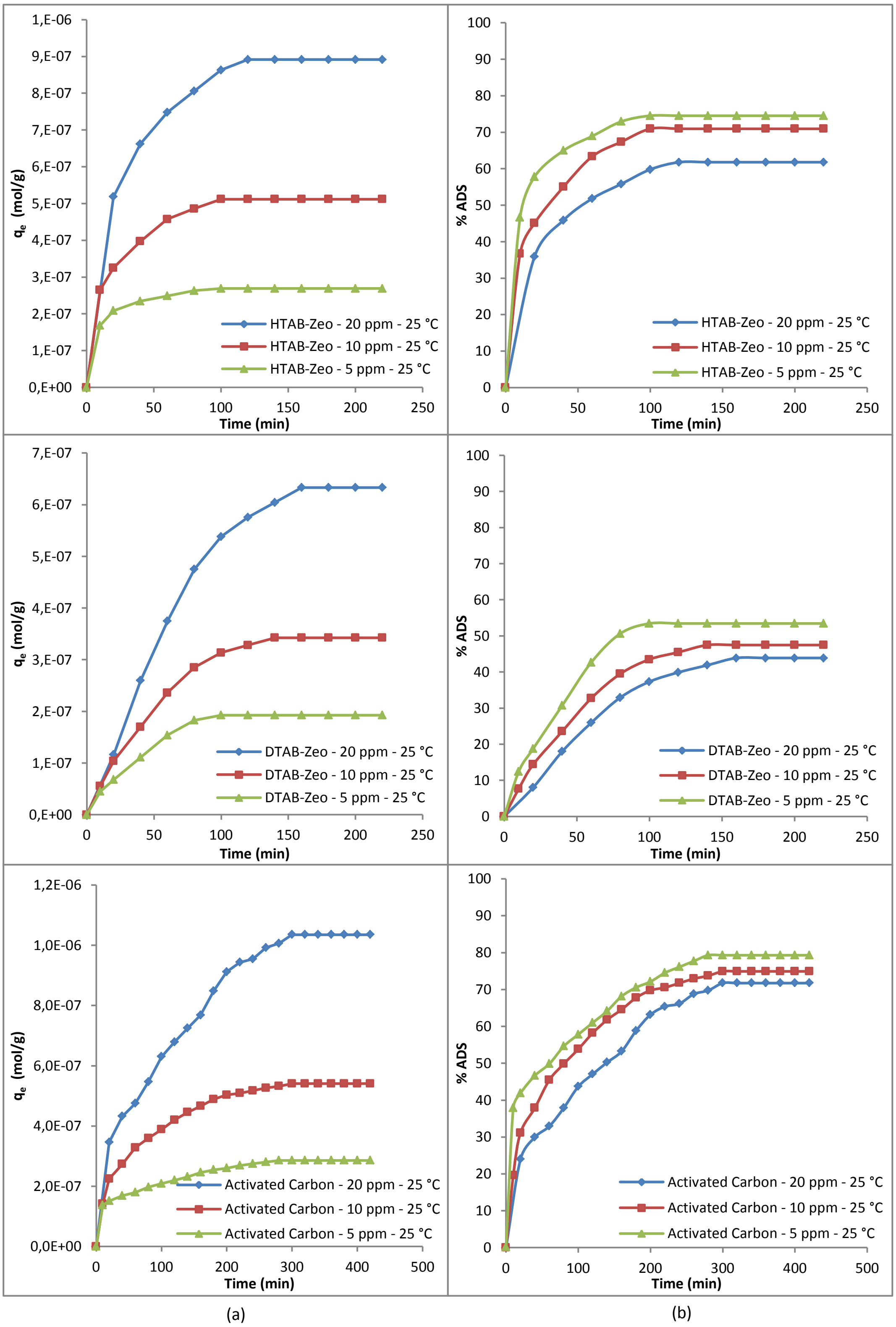


Figure 8.23 Effect of Contact Time and Initial Concentration of Fenitrothion on Adsorption (App. Table C.73, C.76, C.79). (a) Adsorption Capacities of Adsorbents (b) Amount of Adsorbed Pesticide on Adsorbents

Initial concentrations of trifluralin were selected as 5, 10, and 20 mg/L. Adsorption capacities of organo-zeolites and activated carbon are shown in Figure 8.24(a) and amount of adsorbed pesticide at equilibrium concentrations are shown in Figure 8.24(b). The amount of adsorbed pesticide, adsorption capacities of adsorbents and contact time to reach equilibrium concentration are tabulated in Table 8.9.

Table 8.9 The Effect of Initial Trifluralin Concentration on Adsorption

Adsorbent	Initial Concentration of Trifluralin (mg/L)	Equilibrium Time (min)	Adsorption Capacity (mol/g)	Amount of Adsorbed Pesticide (%)
HTAB-Zeo	20	180	9.404×10^{-7}	78.82
	10	160	5.155×10^{-7}	86.42
	5	160	2.756×10^{-7}	92.40
DTAB-Zeo	20	200	6.099×10^{-7}	51.12
	10	200	3.374×10^{-7}	56.56
	5	200	1.816×10^{-7}	60.90
Activated Carbon	20	280	9.695×10^{-7}	81.26
	10	280	5.091×10^{-7}	85.34
	5	280	2.626×10^{-7}	88.05

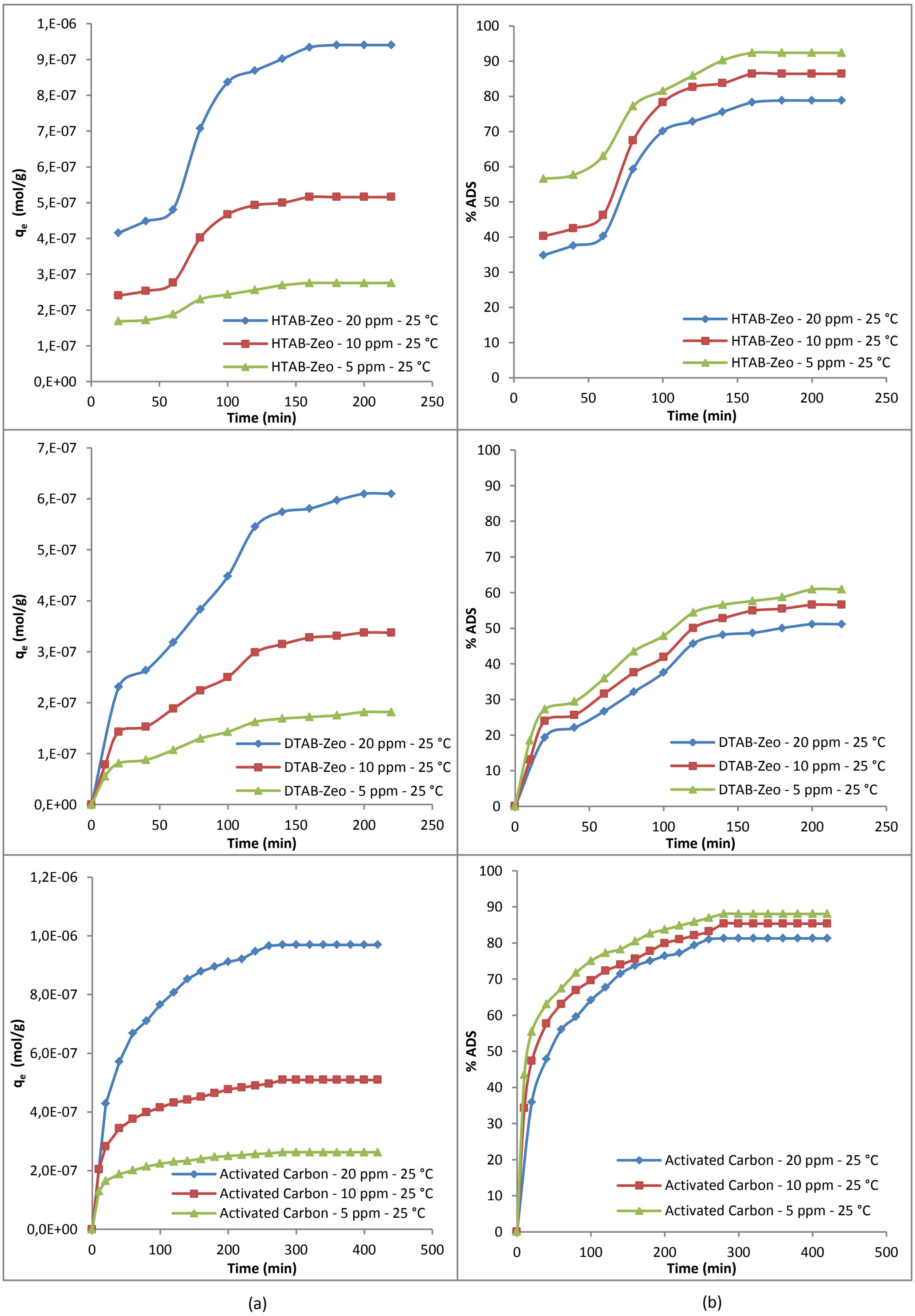


Figure 8.24 Effect of Contact Time and Initial Concentration of Trifluralin on Adsorption (App. Table C.97, C.100, C.103). (a) Adsorption Capacities of Adsorbents (b) Amount of Adsorbed Pesticide on Adsorbents

8.4.2 Effect of Temperature on Adsorption of Pesticides

In order to investigate the effect of temperature on adsorption, experiments were carried out by varying initial pesticide concentrations at different temperatures. Each of pesticides have different chemical properties, so their adsorption by organo-zeolites and activated carbon show different characteristics with increasing temperature.

Effect of temperature on adsorption of 2,4-D on organo-zeolites are shown in Figure 8.25 and Figure 8.26. 2,4-D is an acidic and anionic pesticide and could thus be sorbed by surfactant cation by electrostatic attraction. Surfactant molecules which are gained mobility by increasing temperature removed from the zeolite surface. Therefore, pesticide molecules adsorbed by electrostatic attraction on organo-zeolite surface removed from the surface with increasing temperature. As it is is seen from the figures, adsorbed pesticide on organo-zeolite is decreased with increasing temperature.

Adsorption experiments performed with organo-zeolites have shown that, adsorption capacity of DTAB-Zeolite is lower than that of HTAB-Zeolite. It may be due to weak hydrophobic character of the DTAB-Zeolite than HTAB-zeolite.

Data obtained from adsorption experiments performed with organo-zeolites are given in Table 8.10.

Effect of temperature on adsorption of 2,4-D onto activated carbon at different temperatures is shown in Figure 8.27. As it is seen from Figure 8.27(a), the amount of adsorbed pesticide on activated carbon is increasing with increasing temperature. This increase in adsorption capacity of activated carbon at high temperature may be explained by enlargement of pore size or creation of some new active sites on the adsorbent surface due to the bond rupture.

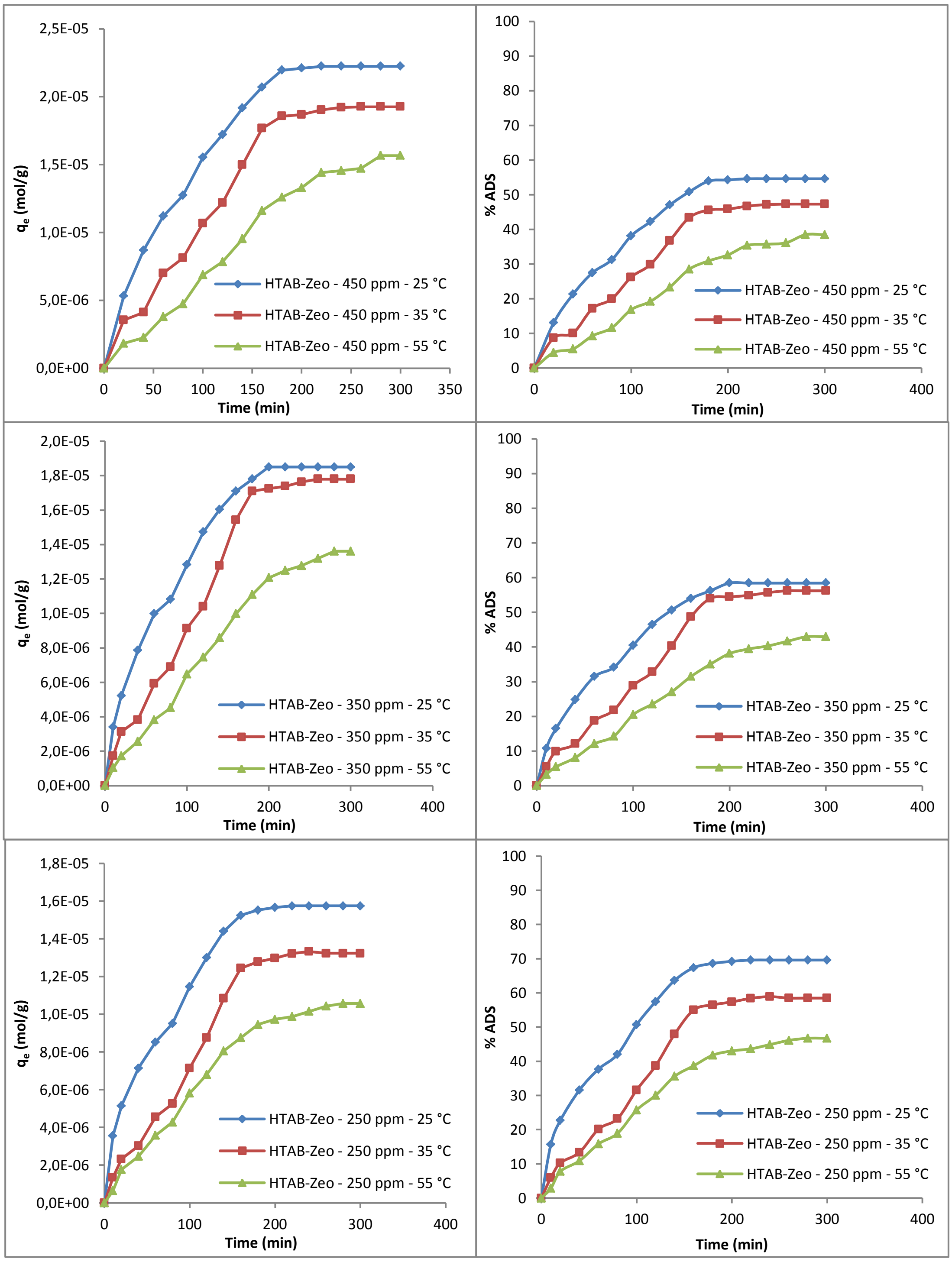
Data obtained from adsorption experiments performed with activated carbon are given in Table 8.11.

Table 8.10 Adsorption of 2,4-D on Organo-zeolites at Different Temperature

Adsorbents	Temperature (°C)	Initial Conc. C_o (mg/L)	Eq. Time (min.)	q_e (mol/g)	% ADS
HTAB - Zeo	25° C	450	220	2.224×10^{-5}	54.62
		350	200	1.850×10^{-5}	58.42
		250	220	1.574×10^{-5}	69.60
	35° C	450	260	1.926×10^{-5}	47.30
		350	260	1.78×10^{-5}	56.21
		250	260	1.323×10^{-5}	58.47
	55° C	450	280	1.567×10^{-5}	38.48
		350	280	1.361×10^{-5}	42.97
		250	280	1.057×10^{-5}	46.73
DTAB - Zeo	25° C	450	140	8.539×10^{-6}	20.97
		350	140	7.878×10^{-6}	24.88
		250	140	6.098×10^{-6}	26.96
	35° C	450	160	7.001×10^{-6}	17.20
		350	160	6.061×10^{-6}	19.14
		250	160	4.840×10^{-6}	21.40
	55° C	450	180	4.975×10^{-6}	12.22
		350	180	4.243×10^{-6}	13.40
		250	180	3.233×10^{-6}	14.29

Table 8.11 Adsorption of 2,4-D on Activated Carbon at Different Temperature

	Temperature (°C)	Initial Conc. C_o (mg/L)	Eq. Time (min.)	q_e (mol/g)	% ADS
Activated Carbon	25° C	450	420	2.238×10^{-5}	54.96
		350	400	2.172×10^{-5}	68.57
		250	320	1.620×10^{-5}	71.64
	35° C	450	320	2.545×10^{-5}	62.51
		350	360	2.339×10^{-5}	73.87
		250	300	1.770×10^{-5}	78.25
	55° C	450	300	2.853×10^{-5}	70.06
		350	320	2.395×10^{-5}	75.64
		250	280	1.924×10^{-5}	85.05



(a) (b)

Figure 8.25 Effect of Temperature on Adsorption of 2,4-D onto HTAB-Zeolite (App. Table C.1, C.2, C.3). (a) Adsorption Capacity of HTAB-Zeolite, (b) Adsorption Percentage of 2,4-D on HTAB-Zeolite

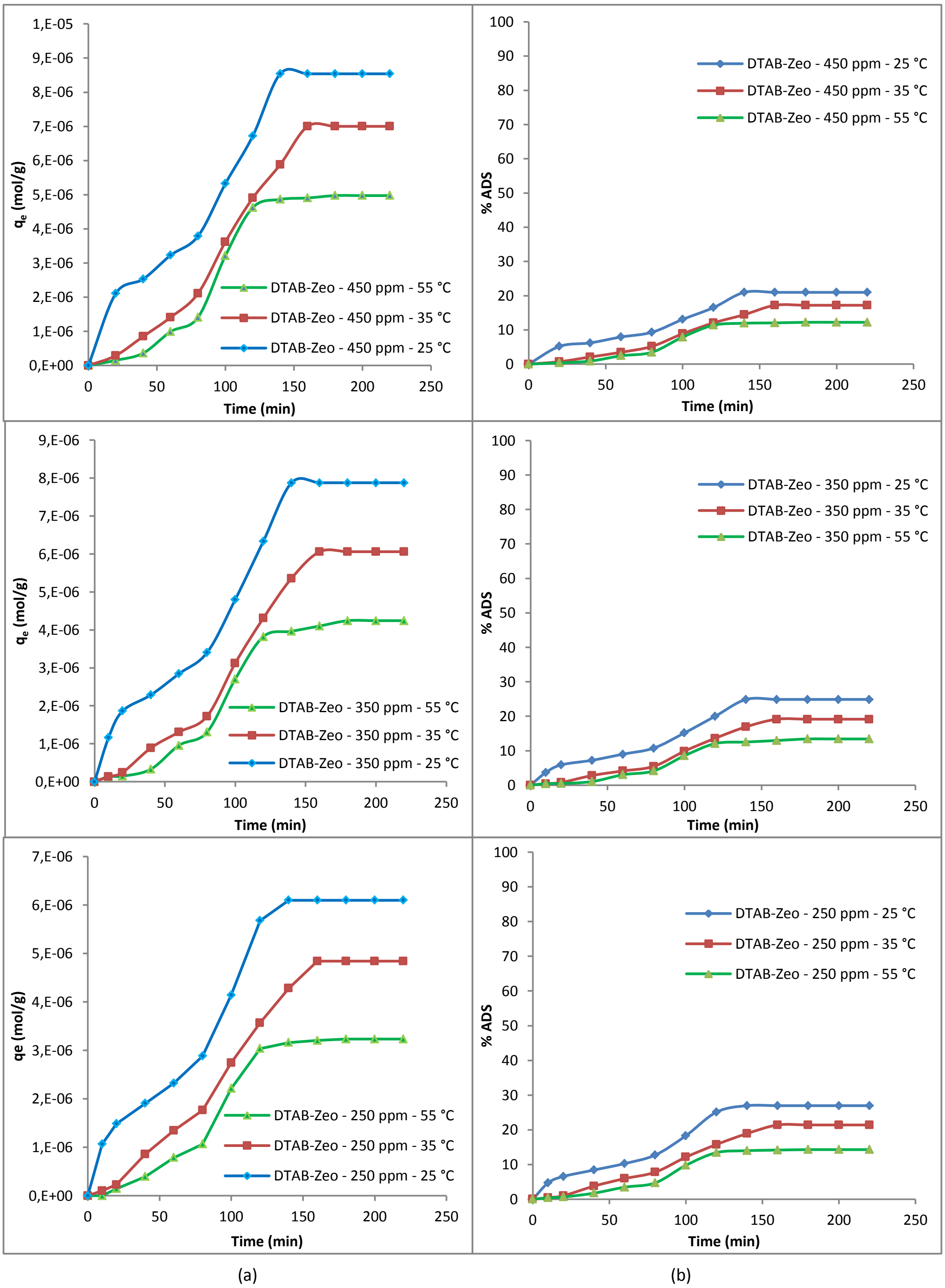


Figure 8.26 Effect of Temperature on Adsorption of 2,4-D onto DTAB-Zeolite (App. Table C.2, C.5, C.8). (a) Adsorption Capacity of DTAB-Zeolite, (b) Adsorption Percentage of 2,4-D on DTAB-Zeolite

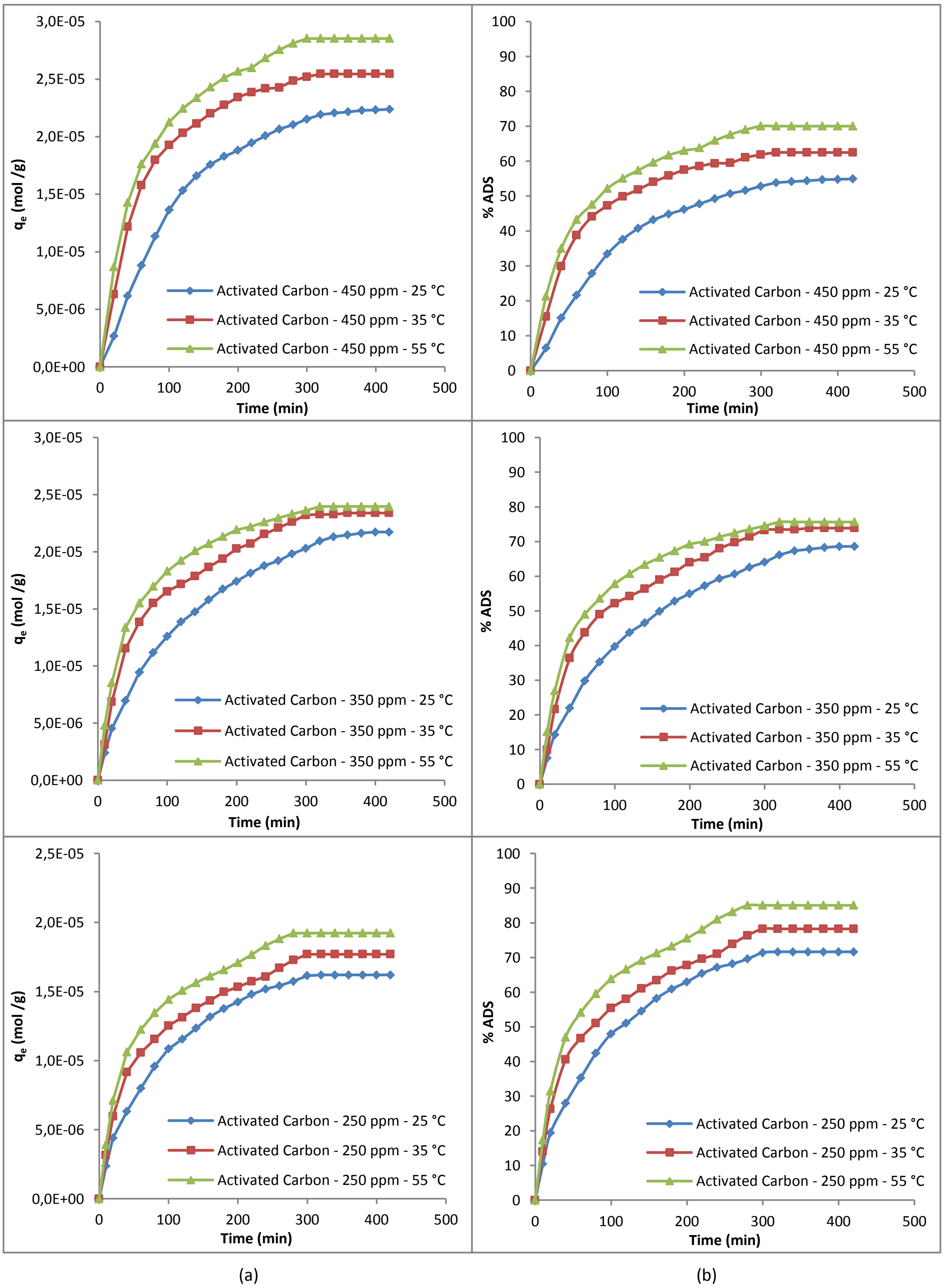


Figure 8.27 Effect of Temperature on Adsorption of 2,4-D onto Activated Carbon (App. Table C.3, C.6, C.9). (a) Adsorption Capacity of Activated Carbon, (b) Adsorption Percentage of 2,4-D on Activated Carbon

Adsorption of propanil on organo-zeolites are shown in Figure 8.28 and Figure 8.29. Propanil is a non-ionic pesticide and could thus be sorbed by surfactant by tail-tail hydrophobic attraction. Surfactant molecules are gained mobility by increasing temperature. Adsorbed cationic surfactant molecules with hydrophobic attraction on zeolite surface removed from the surface by this gained mobility. Therefore, adsorption may be took place between the exposed hydrocarbon chain and pesticide. As it is seen from the figures, adsorbed pesticide on organo-zeolite is increasing with increasing temperature.

Experimental results obtained from propanil adsorption on organo-zeolite show that , adsorption capacity of DTAB-Zeolite is lower than that of HTAB-Zeolite. It can be explained by increasing the active adsorption sites of HTAB-Zeolite with increasing temperature and may be due to weak hydrophobic character of the DTAB-Zeolite rather than HTAB-zeolite.

Data obtained from adsorption experiments performed with organo-zeolites are given in Table 8.12.

Adsorption of propanil on activated carbon at different temperatures is shown in Figure 8.30. As it is seen from Figure 8.30(a), the amount of adsorbed pesticide on activated carbon is increased with increasing temperature. Pore size enlargement or creation of some new active sites on adsorbent surface may result an increase in adsorption capacity of activated carbon at high temperature.

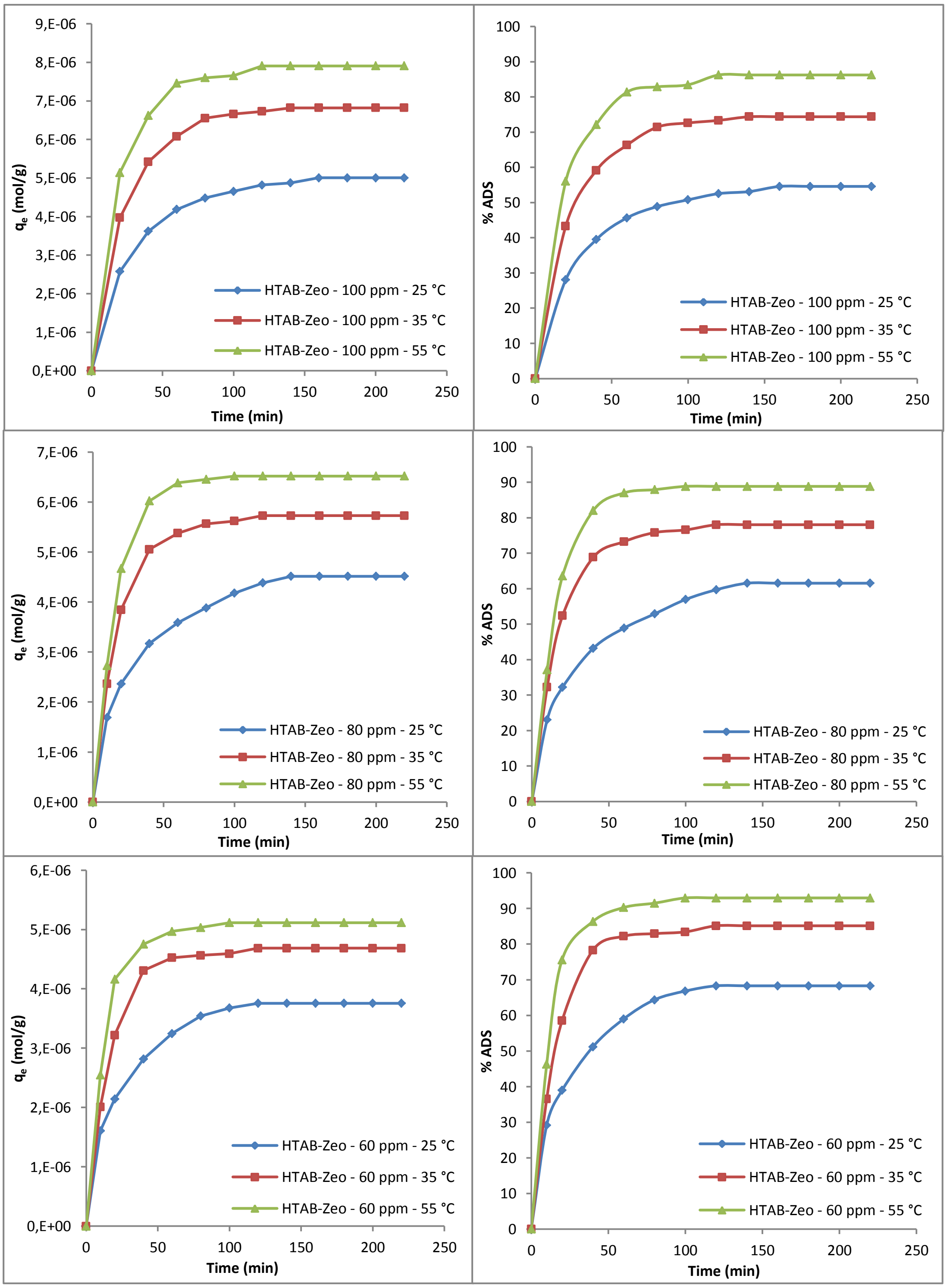
Data obtained from adsorption experiments performed with activated carbon are given in Table 8.13.

Table 8.12 Adsorption of Propanil on Organo-zeolites at Different Temperature

Adsorbents	Temperature (°C)	Initial Conc. C_o (mg/L)	Eq. Time (min.)	q_e (mol/g)	% ADS
HTAB - Zeo	25° C	100	160	5.006×10^{-6}	54.59
		80	140	4.516×10^{-6}	61.56
		60	120	3.758×10^{-6}	68.29
	35° C	100	140	6.821×10^{-6}	74.38
		80	120	5.726×10^{-6}	78.05
		60	120	4.685×10^{-6}	85.15
	55° C	100	120	7.910×10^{-6}	86.25
		80	100	6.519×10^{-6}	88.86
		60	100	5.115×10^{-6}	92.96
DTAB - Zeo	25° C	100	180	2.586×10^{-6}	28.20
		80	160	2.365×10^{-6}	32.24
		60	160	1.916×10^{-6}	34.82
	35° C	100	180	3.527×10^{-6}	38.46
		80	140	3.306×10^{-6}	45.07
		60	120	2.682×10^{-6}	48.74
	55° C	100	140	4.589×10^{-6}	50.04
		80	120	3.979×10^{-6}	54.23
		60	120	3.408×10^{-6}	61.94

Table 8.13 Adsorption of Propanil on Activated Carbon at Different Temperature

	Temperature (°C)	Initial Conc. C_o (mg/L)	Eq. Time (min.)	q_e (mol/g)	% ADS
Activated Carbon	25° C	100	380	5.880×10^{-6}	64.12
		80	380	5.189×10^{-6}	70.72
		60	380	4×10^{-6}	72.96
	35° C	100	360	6.969×10^{-6}	75.99
		80	360	5.861×10^{-6}	79.88
		60	320	4.658×10^{-6}	84.86
	55° C	100	360	8.098×10^{-6}	88.30
		80	360	6.721×10^{-6}	91.61
		60	300	5.102×10^{-6}	92.72



(a) (b)

Figure 8.28 Effect of Temperature on Adsorption of Propanil onto HTAB-Zeolite (App. Table C.25, C.26, C.27). (a) Adsorption Capacity of HTAB-Zeolite, (b) Adsorption Percentage of Propanil on HTAB-Zeolite

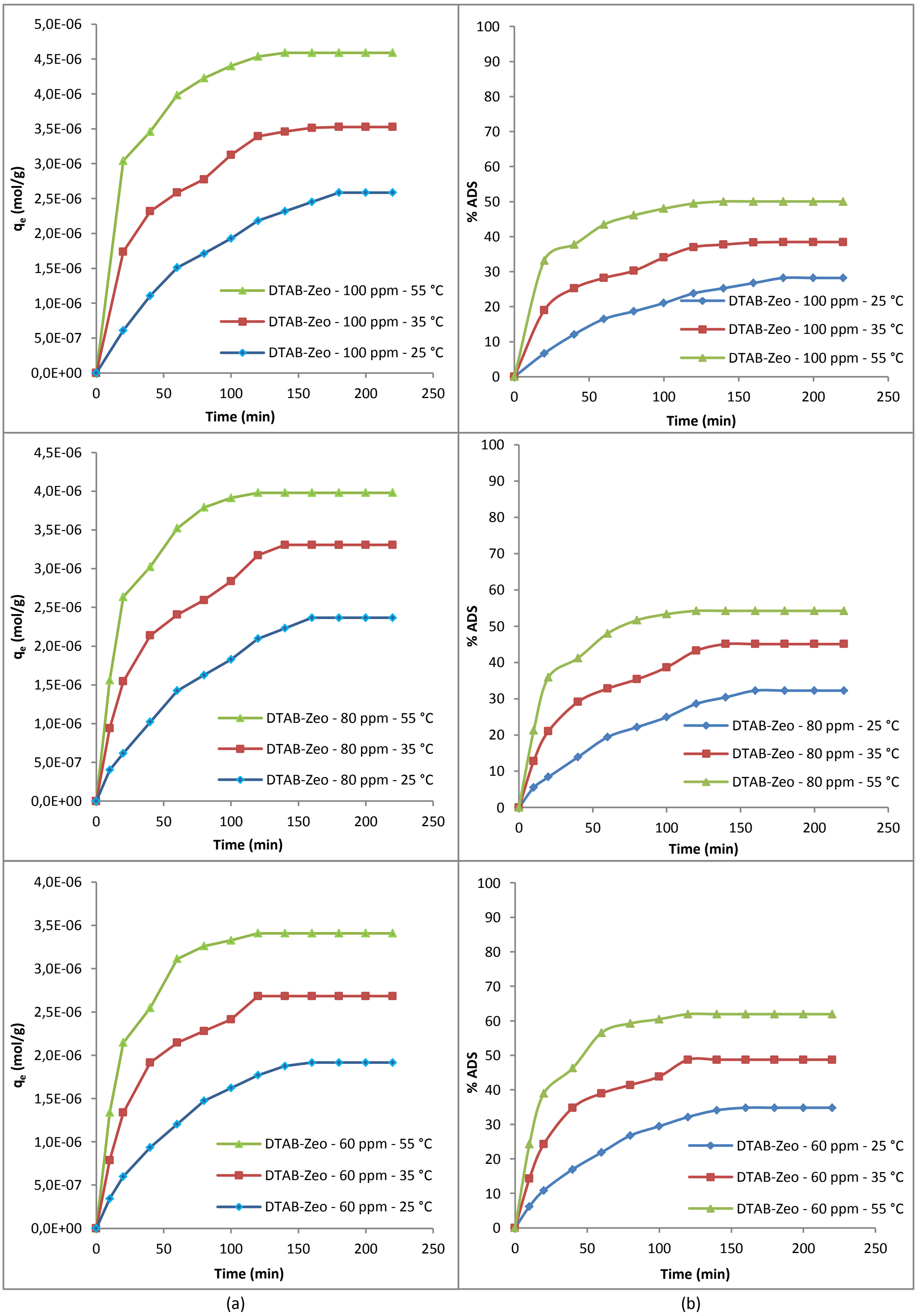


Figure 8.29 Effect of Temperature on Adsorption of Propanil onto DTAB-Zeolite (App. Table C.28, C.29, C.30). (a) Adsorption Capacity of DTAB-Zeolite, (b) Adsorption Percentage of Propanil on DTAB-Zeolite

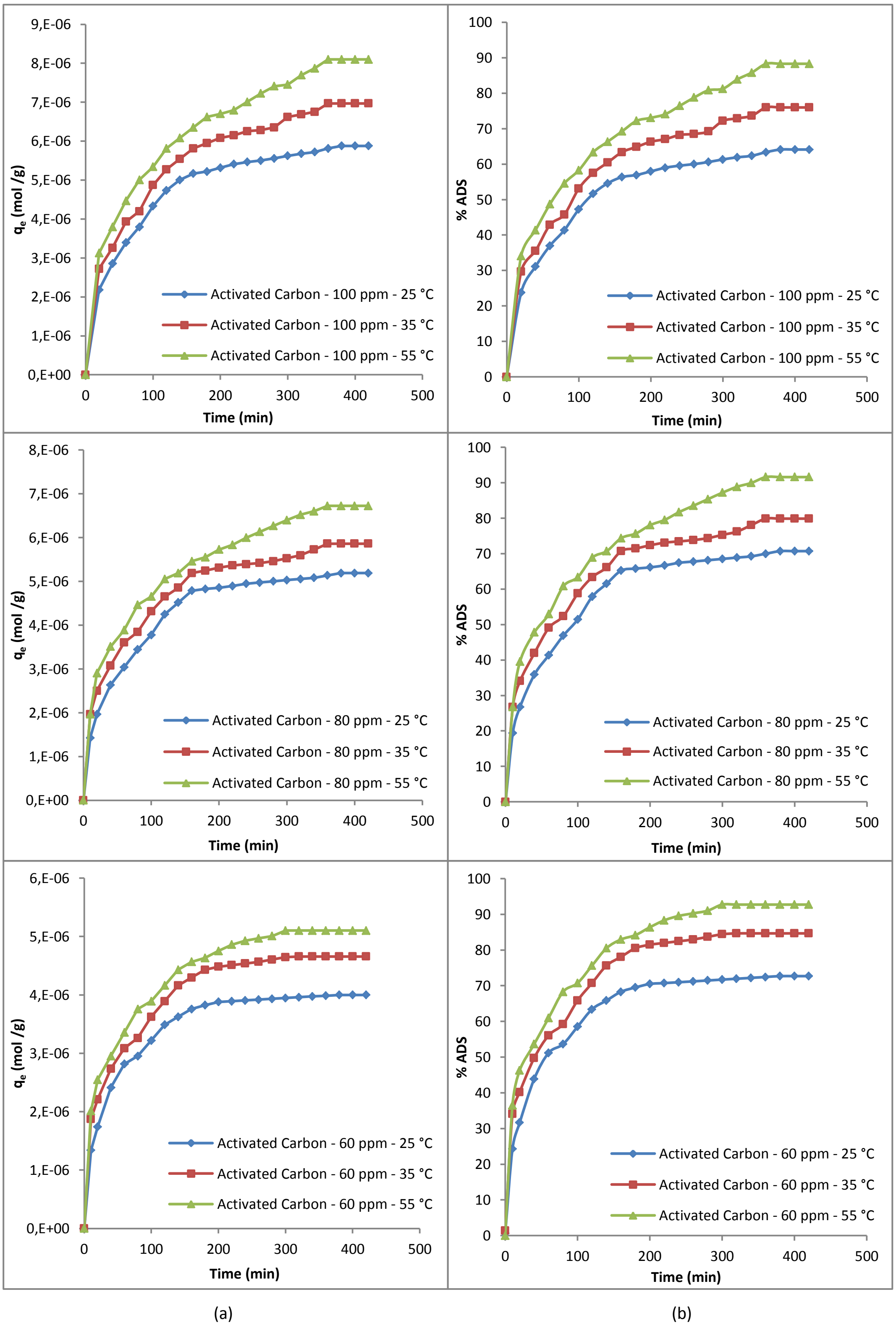


Figure 8.30 Effect of Temperature on Adsorption of Propanil onto Activated Carbon (App. Table C.31, C.32, C.33). (a) Adsorption Capacity of Activated Carbon, (b) Adsorption Percentage of Propanil on Activated Carbon

Adsorption of diazinon on organo-zeolites are shown in Figure 8.31 and Figure 8.32.

Diazinon is relatively water soluble, moderately mobile and persistent in soil. It degrades rapidly in plants, with half-time persistence usually less than 14 days; however, persistence increases as temperature decreases, and is longer in crops with a high oil content (Eisler, 1986).

Diazinon is a non-ionic pesticide and could thus be sorbed by surfactant by tail-tail hydrophobic attraction. Diazinon molecules are rapidly hydrolyzed with increasing temperature. Although, surfactant molecules were gained mobility and created a new active adsorption sites on the organo-zeolite surface by increasing temperature, adsorption capacity of organo-zeolite is decreasing because of the degredation of pesticide with increasing temperature.

Data obtained from adsorption experiments performed with organo-zeolites are given in Table 8.14.

Adsorption of diazinon on activated carbon at different temperatures is shown in Figure 8.33. As it is seen from Figure 8.33(a), the amount of adsorbed pesticide on activated carbon is decreased with increasing temperature.

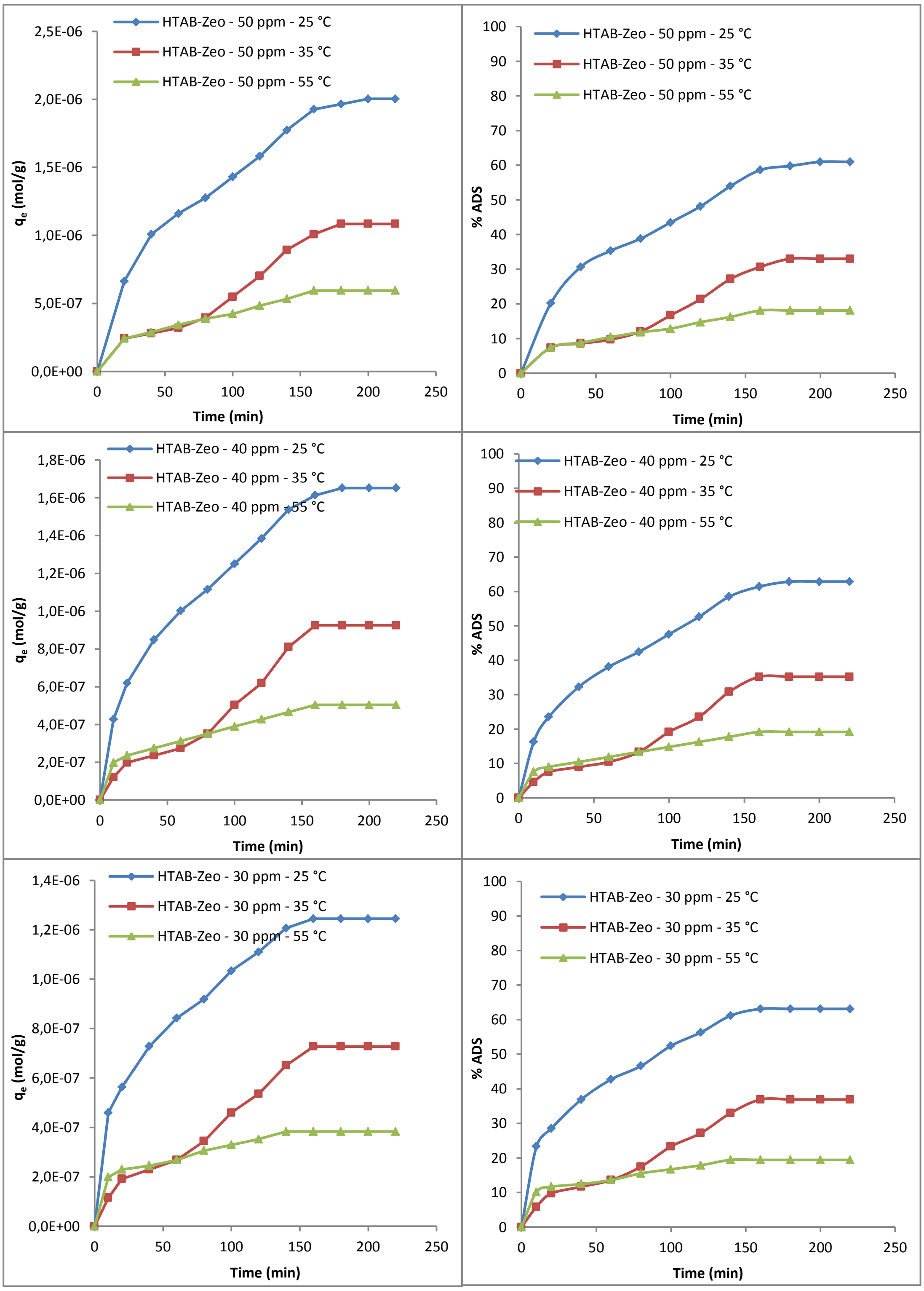
Data obtained from adsorption experiments performed with activated carbon are given in Table 8.15.

Table 8.14 Adsorption of Diazinon on Organo-zeolites at Different Temperature

	Temperature (°C)	Initial Conc. C_o (mg/L)	Eq. Time (min.)	q_e (mol/g)	% ADS
HTAB - Zeo	25° C	50	200	2.003×10^{-6}	60.97
		40	180	1.652×10^{-6}	62.86
		30	160	1.244×10^{-6}	63.11
	35° C	50	180	1.085×10^{-6}	33.01
		40	160	9.251×10^{-7}	35.19
		30	160	7.273×10^{-7}	36.89
	55° C	50	160	5.946×10^{-7}	18.10
		40	160	5.040×10^{-7}	19.17
		30	140	3.828×10^{-7}	19.42
DTAB - Zeo	25° C	50	200	1.085×10^{-6}	33.01
		40	200	9.634×10^{-7}	36.65
		30	200	7.618×10^{-7}	38.64
	35° C	50	180	6.635×10^{-7}	20.19
		40	180	5.423×10^{-7}	20.63
		30	180	4.976×10^{-7}	25.24
	55° C	50	160	3.955×10^{-7}	12.04
		40	140	3.509×10^{-7}	13.35
		30	140	2.718×10^{-7}	13.79

Table 8.15 Adsorption of Diazinon onActivated Carbon at Different Temperature

	Temperature (°C)	Initial Conc. C_o (mg/L)	Eq. Time (min.)	q_e (mol/g)	% ADS
Activated Carbon	25° C	50	320	2.271×10^{-6}	69.13
		40	300	1.897×10^{-6}	72.18
		30	300	1.474×10^{-6}	74.76
	35° C	50	300	1.467×10^{-6}	44.66
		40	280	1.193×10^{-6}	45.39
		30	260	1.034×10^{-6}	52.43
	55° C	50	300	1.008×10^{-6}	30.68
		40	280	8.868×10^{-7}	33.74
		30	260	6.890×10^{-7}	34.95



(a) (b)

Figure 8.31 Effect of Temperature on Adsorption of Diazinon onto HTAB-Zeolite (App. Table C.49, C.50, C.51). (a) Adsorption Capacity of HTAB-Zeolite, (b) Adsorption Percentage of Diazinon on HTAB-Zeolite

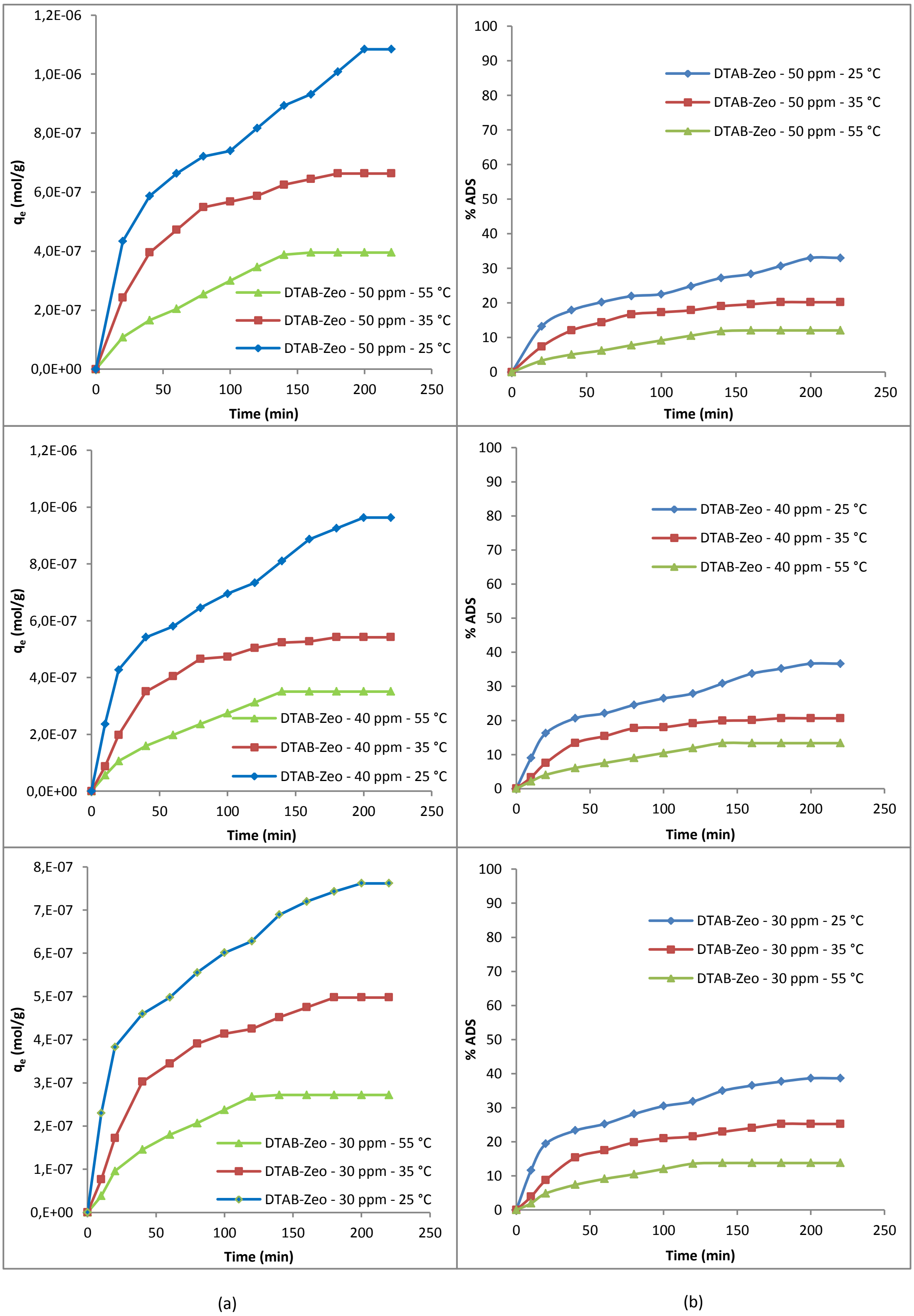
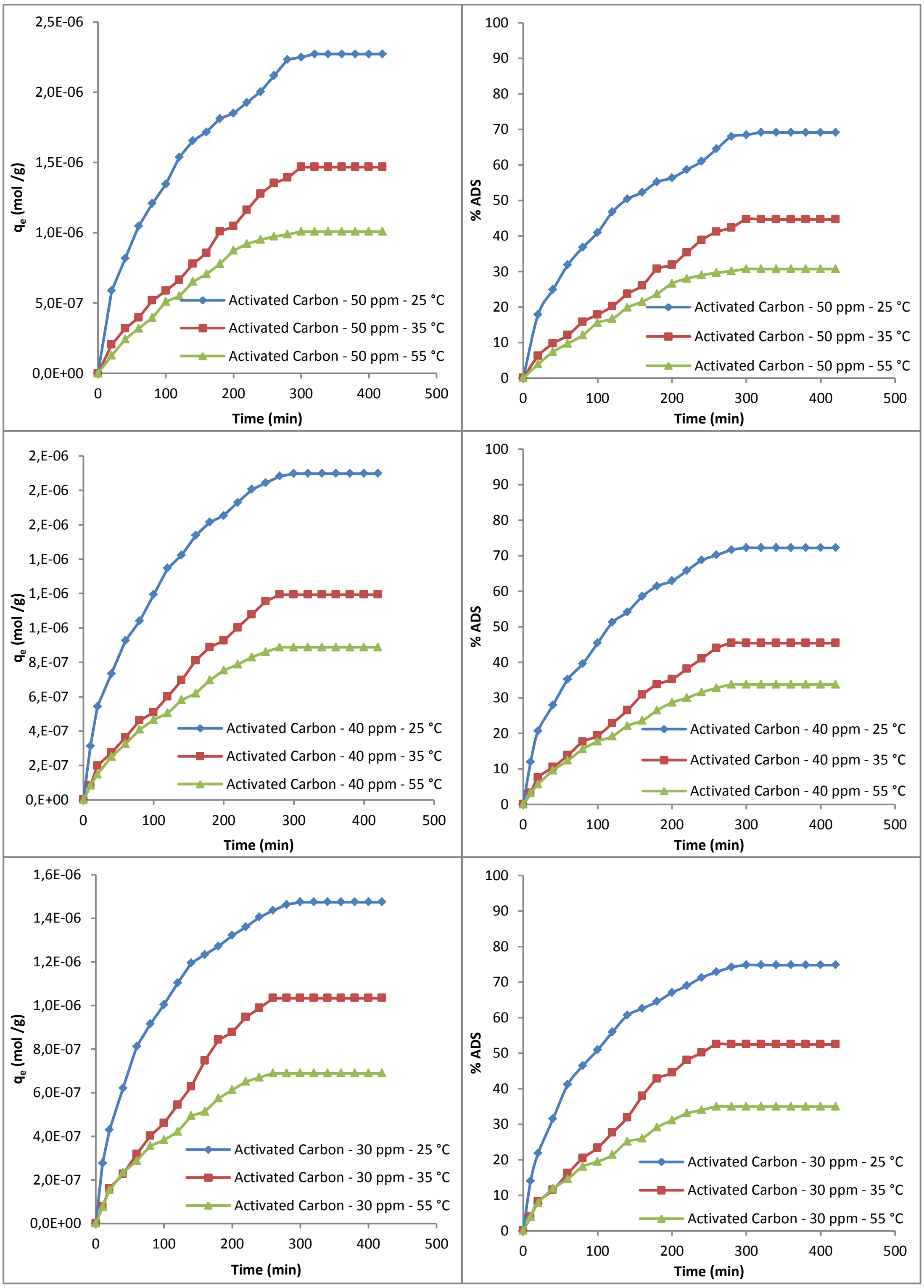


Figure 8.32 Effect of Temperature on Adsorption of Diazinon onto DTAB-Zeolite (App. Table C.52, C.53, C.54). (a) Adsorption Capacity of DTAB-Zeolite, (b) Adsorption Percentage of Diazinon on DTAB-Zeolite



(a) (b)

Figure 8.33 Effect of Temperature on Adsorption of Diazinon onto Activated Carbon (App. Table C.55, C.56, C.57). (a) Adsorption Capacity of Activated Carbon, (b) Adsorption Percentage of Diazinon on Activated Carbon

Adsorption of fenitrothion on organo-zeolites are shown in Figure 8.34 and Figure 8.35.

Fenitrothion is an organophosphorus insecticide and is widely used in the world against insects. It degrades fairly rapidly in soil with a half-life of less than one week in non-sterile muck, sandy loam soils. This pesticide is moderately mobile in a variety of soils ranging from sandy loam to clay.

Fenitrothion is completely stable for two years if stored at temperatures between 20 and 25°C. Storage temperature should not exceed 40°C. The thermal stability of this compound is low, and when it is heated above 100°C it undergoes Pishchemuka isomerization and may decompose explosively. As it is seen from figures, adsorption capacity of organo-zeolite is decreased with increasing temperature.

Data obtained from adsorption experiments performed with organo-zeolites are given in Table 8.16.

Adsorption of fenitrothion on activated carbon at different temperatures is shown in Figure 8.36. As it is seen from Figure 8.36(a), the amount of adsorbed pesticide on activated carbon is decreased with increasing temperature. Fenitrothion adsorption is exothermic thus adsorption capacity of activated carbon is decreasing with increasing temperature.

Data obtained from adsorption experiments performed with activated carbon are given in Table 8.17.

Table 8.16 Adsorption of Fenitrothion on Organo-zeolites at Different Temperature

	Temperature (°C)	Initial Conc. C_o (mg/L)	Eq. Time (min.)	q_e (mol/g)	% ADS
HTAB - Zeo	25° C	20	120	8.916×10^{-7}	61.79
		10	100	5.118×10^{-7}	70.95
		5	100	2.688×10^{-7}	74.53
	35° C	20	100	5.671×10^{-7}	39.30
		10	80	3.424×10^{-7}	47.46
		5	80	1.770×10^{-7}	49.06
	55° C	20	80	4.465×10^{-7}	30.95
		10	80	2.563×10^{-7}	35.52
		5	80	1.454×10^{-7}	40.30
DTAB - Zeo	25° C	20	160	6.331×10^{-7}	43.88
		10	140	3.424×10^{-7}	47.46
		5	100	1.927×10^{-7}	53.43
	35° C	20	120	4.609×10^{-7}	31.94
		10	100	2.563×10^{-7}	35.52
		5	80	1.368×10^{-7}	37.91
	55° C	20	100	3.747×10^{-7}	25.97
		10	100	1.902×10^{-7}	26.37
		5	80	1.109×10^{-7}	30.75

Table 8.17 Adsorption of Fenitrothion on Activated Carbon at Different Temperature

	Temperature (°C)	Initial Conc. C_o (mg/L)	Eq. Time (min.)	q_e (mol/g)	% ADS
Activated Carbon	25° C	20	300	1.035×10^{-6}	71.74
		10	300	5.405×10^{-7}	74.93
		5	280	2.861×10^{-7}	79.30
	35° C	20	260	6.331×10^{-7}	43.88
		10	260	3.281×10^{-7}	45.47
		5	260	1.827×10^{-7}	50.65
	55° C	20	240	5.183×10^{-7}	35.92
		10	220	2.850×10^{-7}	39.50
		5	220	1.540×10^{-7}	42.69

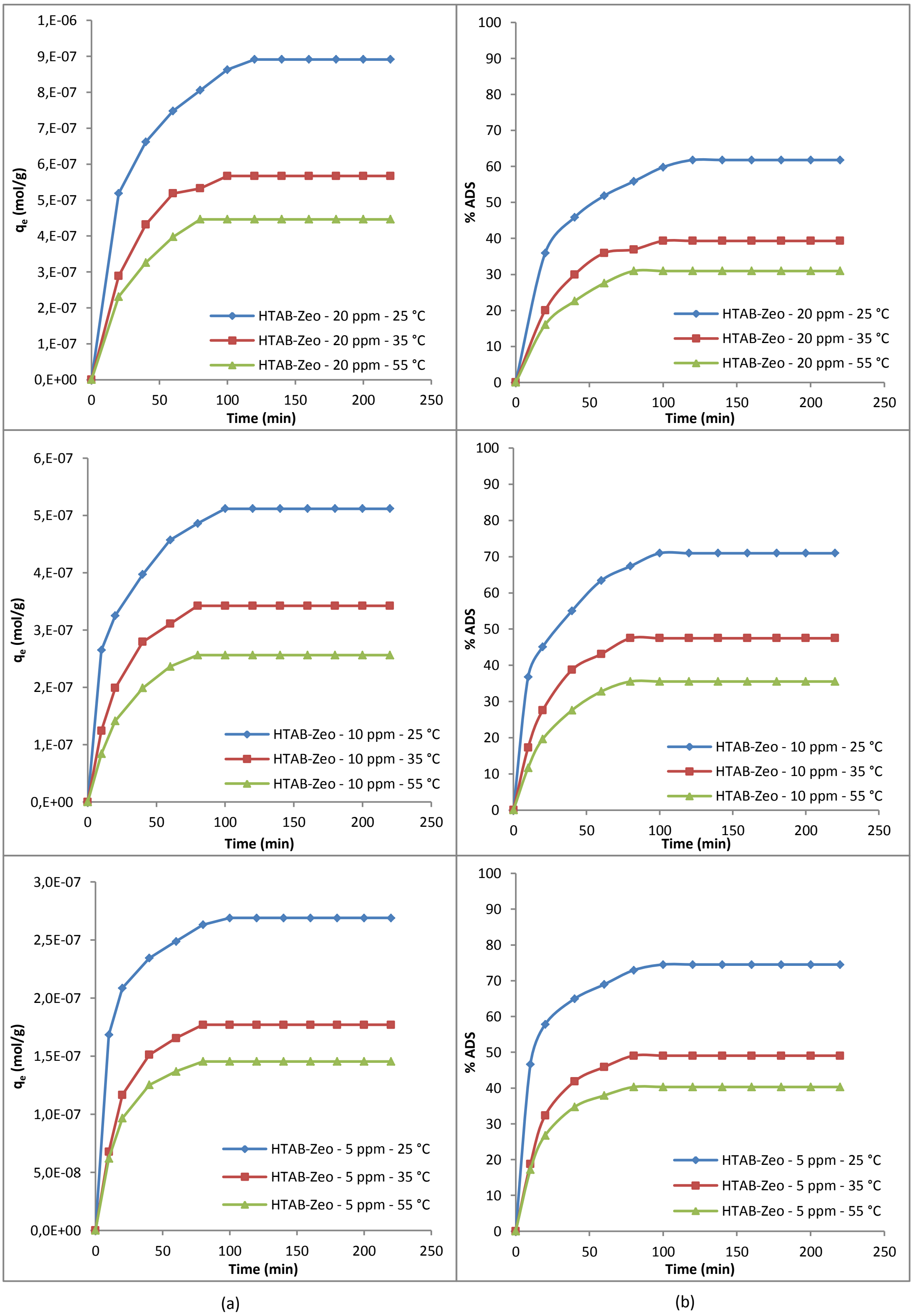


Figure 8.34 Effect of Temperature on Adsorption of Fenitrothion onto HTAB-Zeolite (App. Table C.73, C.74, C.75). (a) Adsorption Capacity of HTAB-Zeolite, (b) Adsorption Percentage of Fenitrothion on HTAB-Zeolite

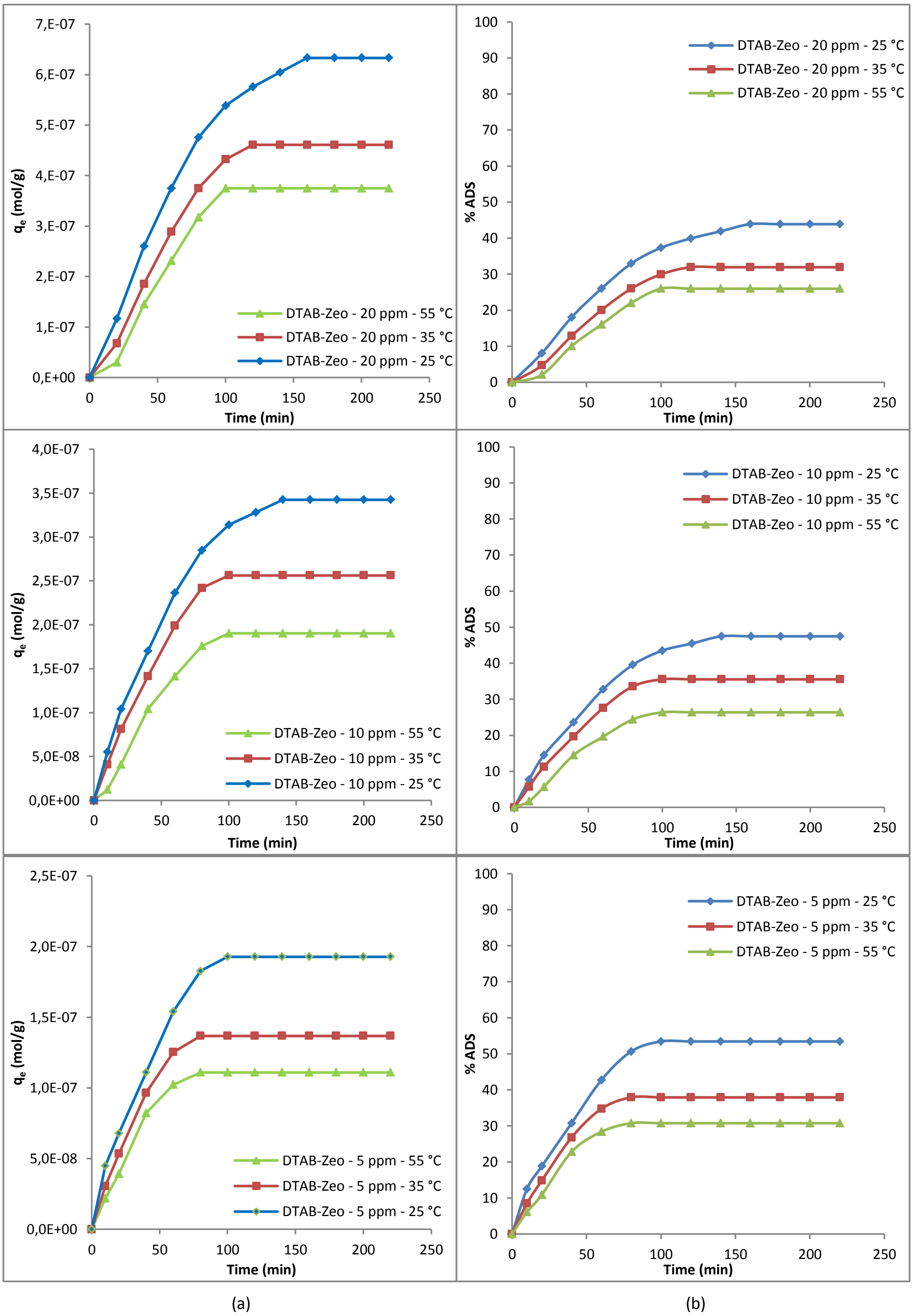


Figure 8.35 Effect of Temperature on Adsorption of Fenitrothion onto DTAB-Zeolite (App. Table C.76, C.77, C.78). (a) Adsorption Capacity of DTAB-Zeolite, (b) Adsorption Percentage of Fenitrothion on DTAB-Zeolite

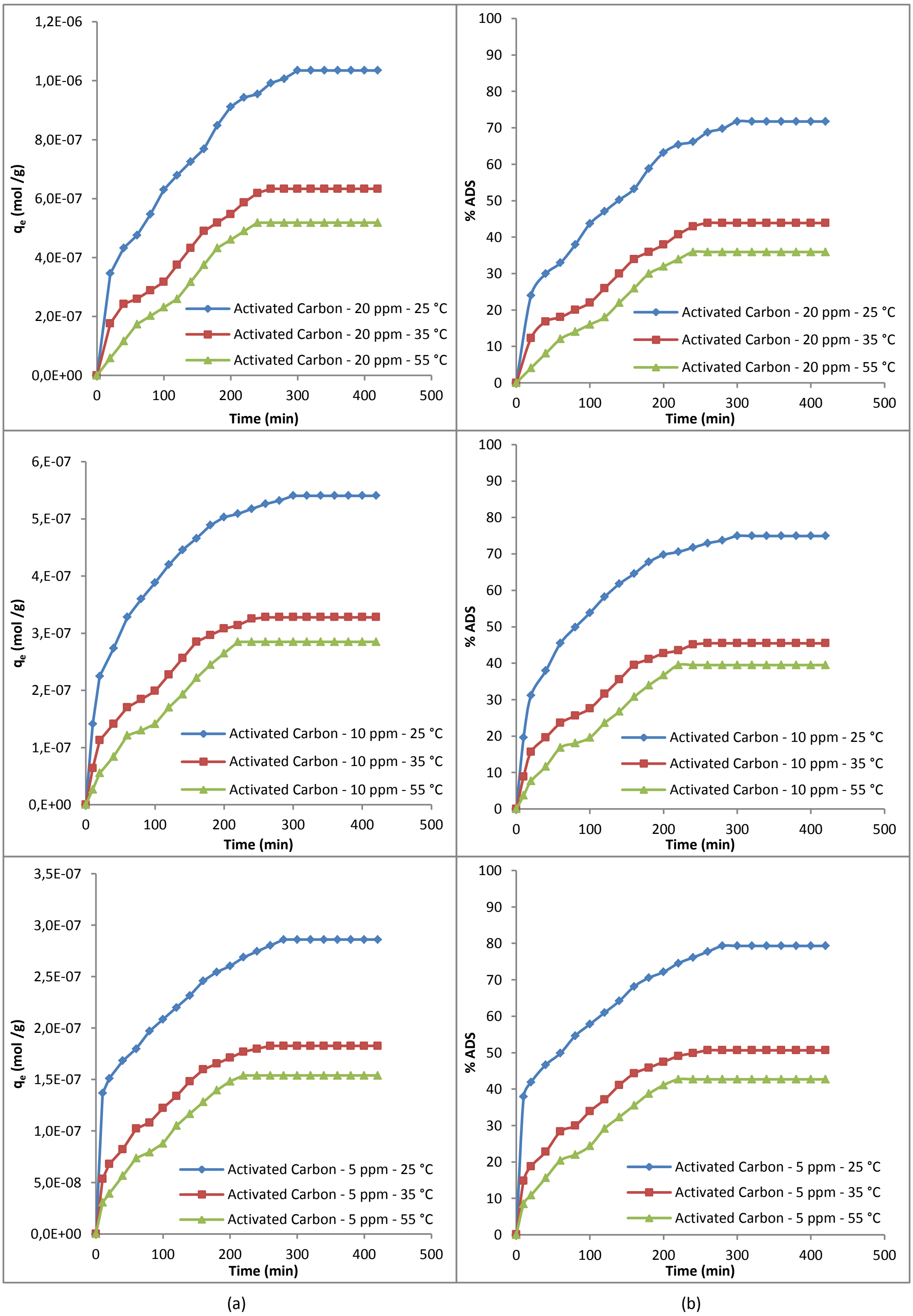


Figure 8.36 Effect of Temperature on Adsorption of Fenitrothion onto Activated Carbon (App. Table C.79, C.80, C.81). (a) Adsorption Capacity of Activated Carbon, (b) Adsorption Percentage of Fenitrothion on Activated Carbon

Adsorption of trifluralin on organo-zeolites are shown in Figure 8.37 and Figure 8.38.

Trifluralin is a dinitroaniline pre-emergence herbicide. Dinitroaniline group pesticides do not move much in the soil, but remain where they are applied. Trifluralin is strongly adsorbed on soil and almost insoluble in water. Hollist and Foy (1971) found that soil adsorption of trifluralin was directly related to the amount of organic matter and clay present in the soil. Hamaker and Thompson suggested that pesticides whose molecules have non-polar regions of significant size relative to polar regions, such as dinitroanilines, are likely to adsorb into the hydrophobic regions of adsorbent surfaces by means of the Van der Waals forces reinforced by hydrophobic bonding.

Trifluralin may enter the aquatic environment predominantly via diffuse sources resulting from its recommended use, e.g. in agricultural run-off bound mainly to soil particles. Industrial discharges, accidental spillages during transport, storage and use are potential point sources of trifluralin contamination (UK SACs, n.d.).

As it is seen from Figure 8.37 and Figure 8.38, trifluralin adsorption capacity of organo-zeolite is increased with increasing temperature.

Data obtained from adsorption experiments performed with organo-zeolites are given in Table 8.18.

Adsorption of trifluralin on activated carbon at different temperatures is shown in Figure 8.39. As it is seen from Figure 8.39(a), the amount of adsorbed pesticide on activated carbon is increased with increasing temperature. Trifluralin adsorbs to the soil organic matter easily. This increasing in adsorption capacity of activated carbon at high temperature may be explained by creation of some new active sites on the adsorbent surface.

Data obtained from adsorption experiments performed with activated carbon are given in Table 8.19.

Table 8.18 Adsorption of Trifluralin on Organo-zeolites at Different Temperature

	Temperature (°C)	Initial Conc. C_o (mg/L)	Eq. Time (min.)	q_e (mol/g)	% ADS
HTAB - Zeo	25° C	20	160	9.339×10^{-7}	78.28
		10	160	5.155×10^{-7}	86.42
		5	160	2.756×10^{-7}	92.40
	35° C	20	120	1.005×10^{-6}	84.25
		10	120	5.317×10^{-7}	89.14
		5	100	2.853×10^{-7}	95.66
	55° C	20	100	1.063×10^{-6}	89.14
		10	100	5.512×10^{-7}	92.40
		5	80	2.918×10^{-7}	97.83
DTAB - Zeo	25° C	20	200	6.009×10^{-7}	51.12
		10	200	3.374×10^{-7}	56.56
		5	200	1.816×10^{-7}	60.90
	35° C	20	180	6.423×10^{-7}	53.84
		10	160	3.536×10^{-7}	59.27
		5	160	1.881×10^{-7}	63.07
	55° C	20	140	7.266×10^{-7}	60.90
		10	140	4.022×10^{-7}	67.42
		5	140	2.108×10^{-7}	70.67

Table 8.19 Adsorption of Trifluralin on Activated Carbon at Different Temperature

	Temperature (°C)	Initial Conc. C_o (mg/L)	Eq. Time (min.)	q_e (mol/g)	% ADS
Activated Carbon	25° C	20	280	9.695×10^{-7}	81.26
		10	280	5.091×10^{-7}	85.34
		5	280	2.626×10^{-7}	88.05
	35° C	20	260	1.028×10^{-6}	86.15
		10	240	5.414×10^{-7}	90.77
		5	240	2.723×10^{-7}	91.31
	55° C	20	220	1.080×10^{-6}	90.50
		10	200	5.544×10^{-7}	92.94
		5	200	2.821×10^{-7}	94.57

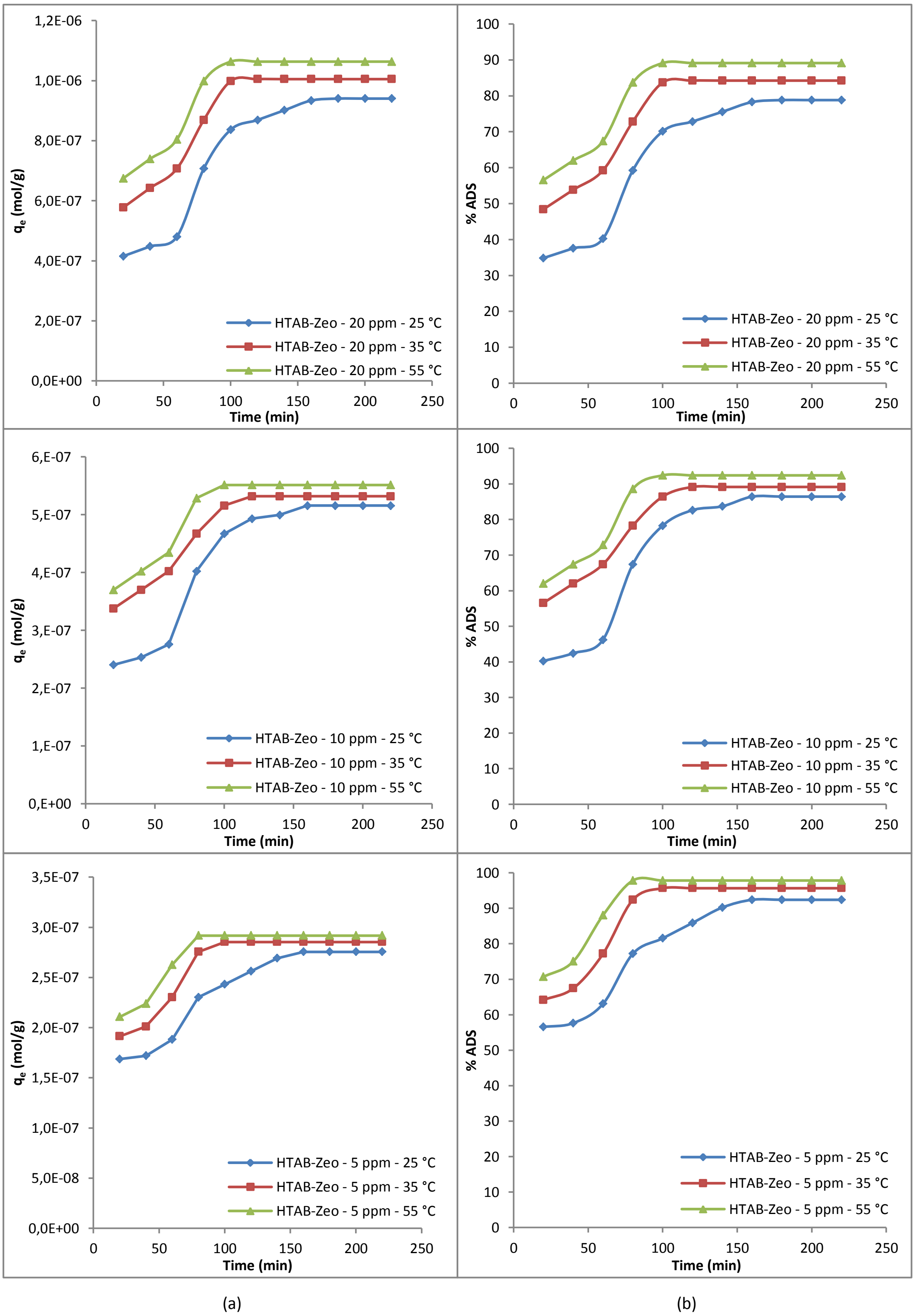


Figure 8.37 Effect of Temperature on Adsorption of Trifluralin onto HTAB-Zeolite (App. Table C.97, C.98, C.99). (a) Adsorption Capacity of HTAB-Zeolite, (b) Adsorption Percentage of Trifluralin on HTAB-Zeolite

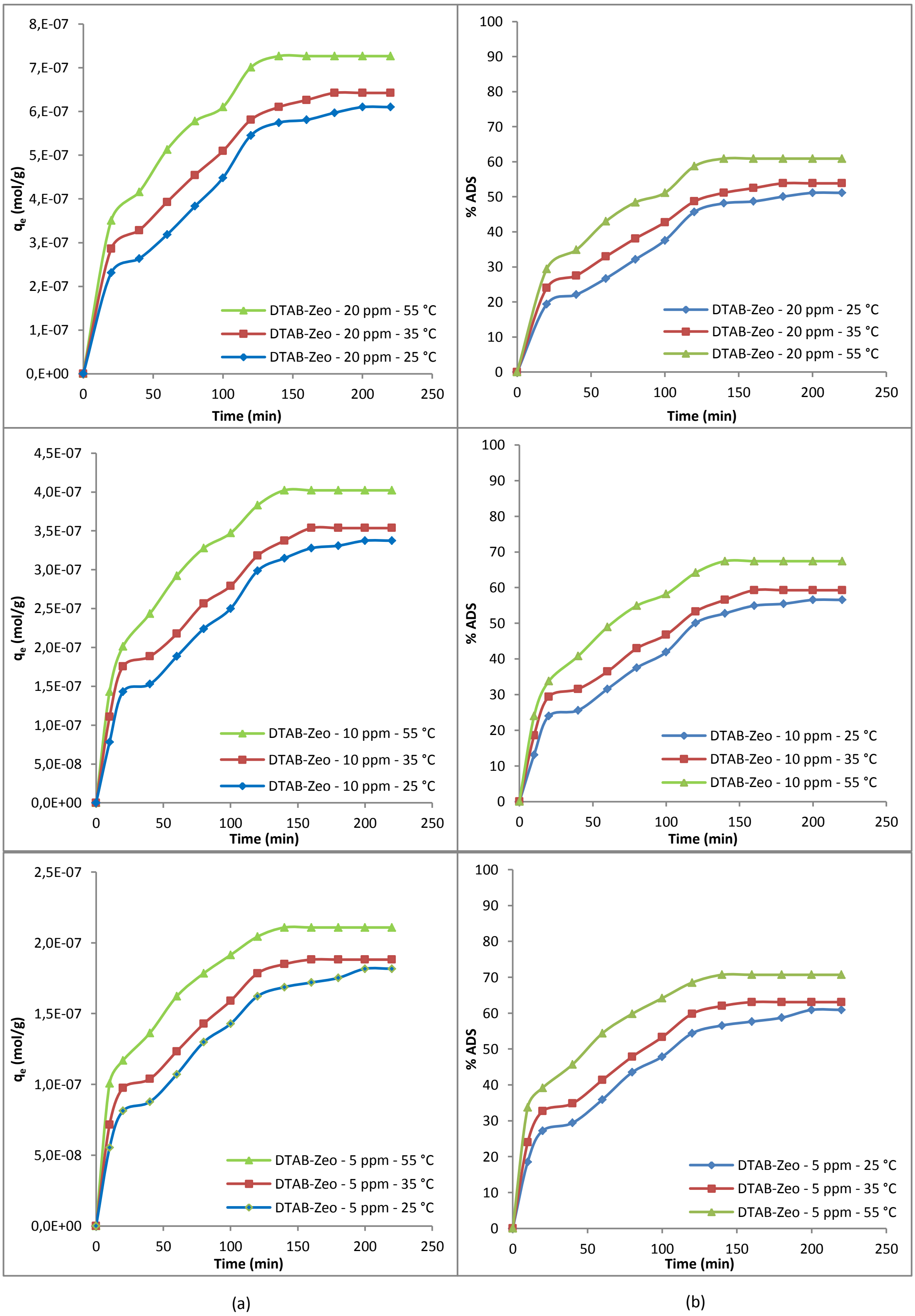


Figure 8.38 Effect of Temperature on Adsorption of Trifluralin onto DTAB-Zeolite (App. Table C.100, C.101, C.102). (a) Adsorption Capacity of DTAB-Zeolite, (b) Adsorption Percentage of Trifluralin on DTAB-Zeolite

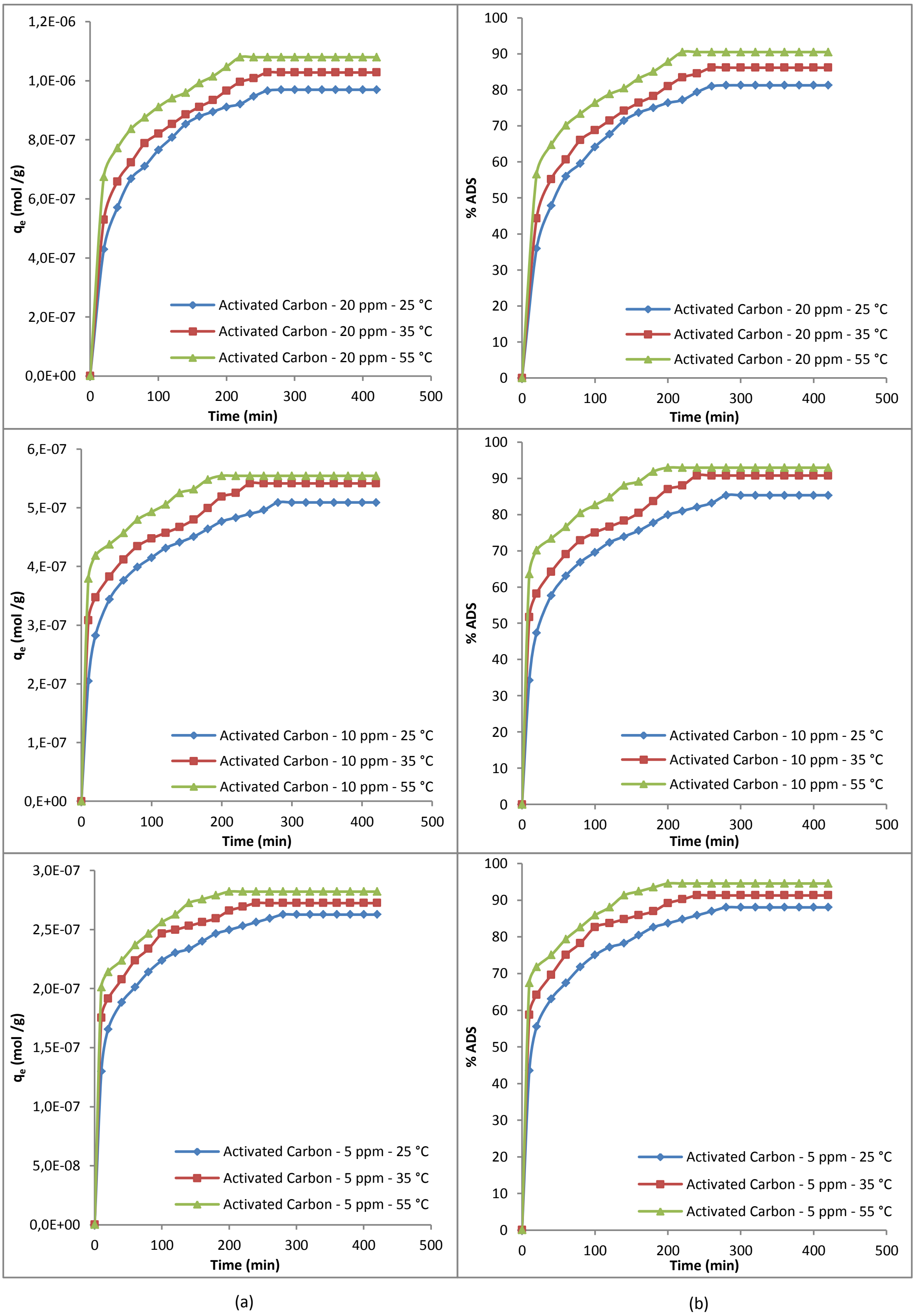


Figure 8.39 Effect of Temperature on Adsorption of Trifluralin onto Activated Carbon (App. Table C.103, C.104, C.105). (a) Adsorption Capacity of Activated Carbon, (b) Adsorption Percentage of Trifluralin on Activated Carbon

8.4.3 Effect of pH on Adsorption of Pesticides

Data obtained from the experiments with different adsorbents in different initial concentrations of pesticide at 25° C have been used in the construction of the adsorption isotherms for pH range from 3 to 11.

Adsorption of 2,4-D on adsorbents are shown in Figure 8.40. It was found that an increase in pH led to a decrease adsorption amount of 2,4-D by adsorbents, and a maximum amount of 2,4-D was adsorbed at pH 3 which is almost equal to its pK_a value (pH 2.64). 2,4-D is a weak acid; therefore increasing the pH increases the ionization of 2,4-D. 10% of the 2,4-D molecules are in an ionized form at pH 3, and almost 100% at pH 9. This indicates that protonated 2,4-D molecules dominating at low pH are more adsorbable than the ionized form

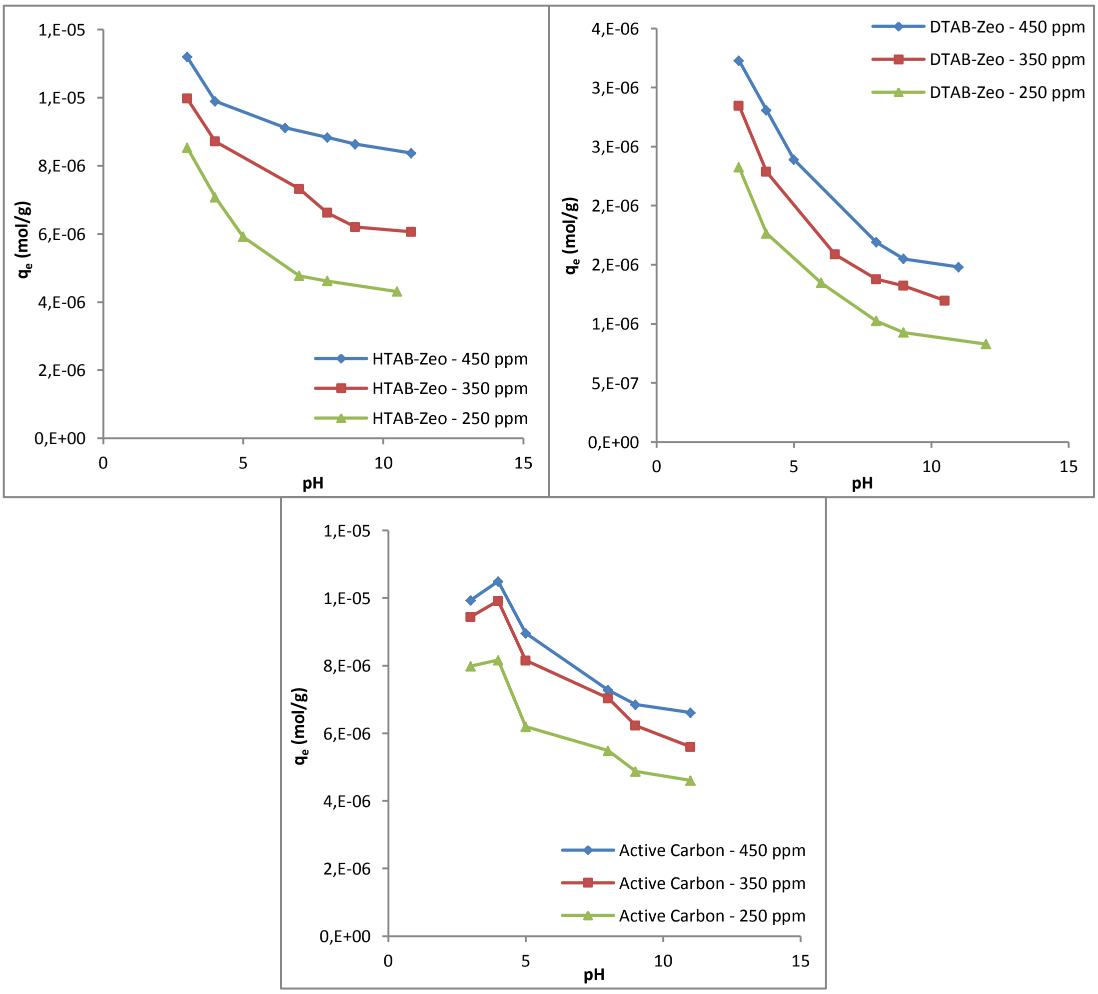


Figure 8.40 Effect of pH on Adsorption of 2,4-D (App. Table C.10, C.11, C.12)

Adsorption of propanil on adsorbents are shown in Figure 8.41. As it is seen from figure, pH of the solution was not effective on the adsorption process of propanil on HTAB-Zeolite and activated carbon. Whereas, adsorption capacity of DTAB-zeolite is decreased with increasing pH of the solution. Maximum amount of propanil was adsorbed at pH 7. Therefore, pH value was chosen as neutral pH for propanil adsorption.

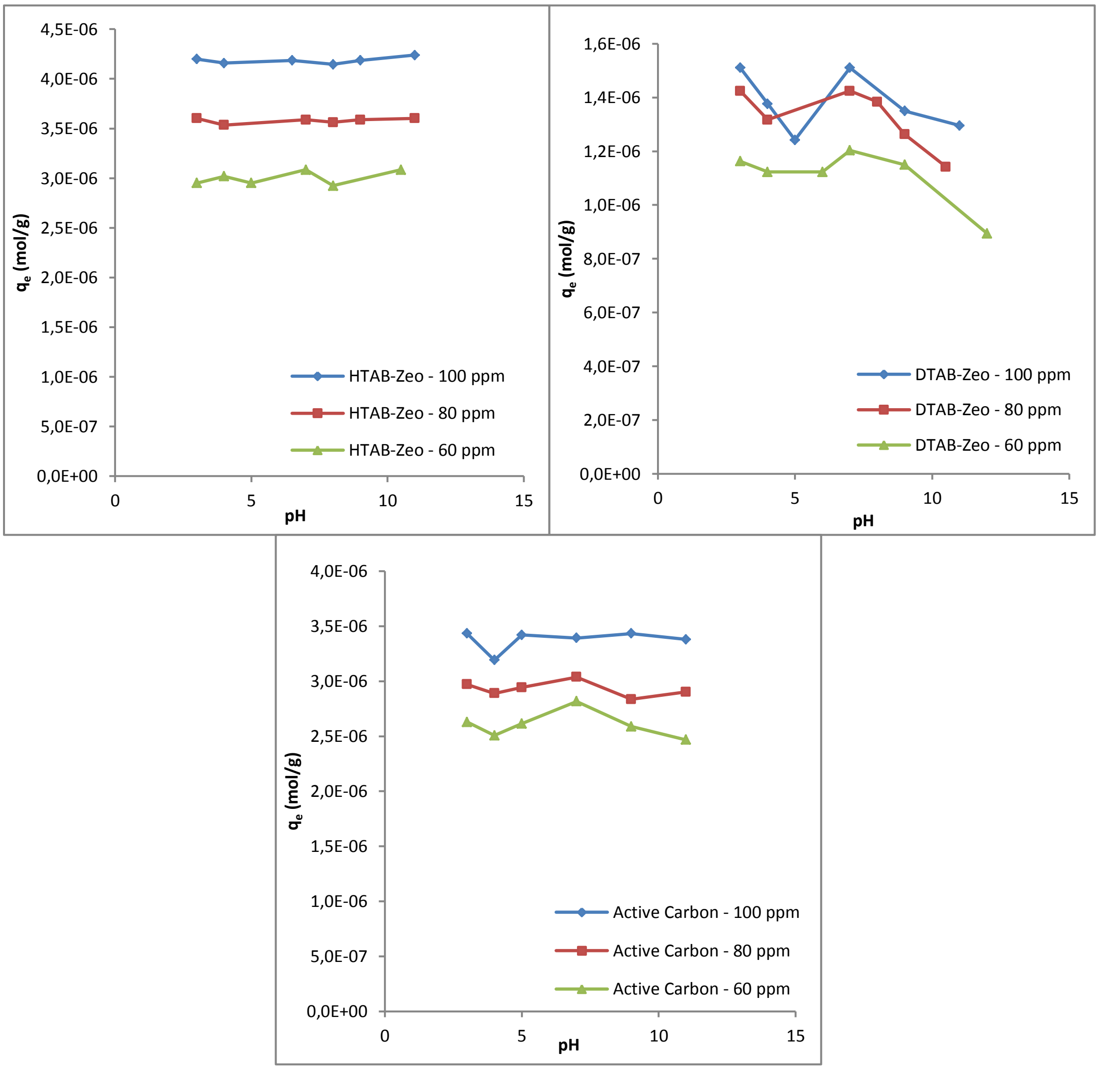


Figure 8.41 Effect of pH on Adsorption of Propanil (App. Table C.34, C.35, C.36)

Adsorption of diazinon on adsorbents are shown in Figure 8.42. It was found that diazinon was rapidly hydrolyzed in low or high pH of medium. Adsorption capacities of three type of adsorbents are increased between pH 3 to 7, and decreased between pH 7 to 11. Maximum amount of diazinon was adsorbed at pH 7. Therefore, pH value was chosen as neutral pH for diazinon adsorption.

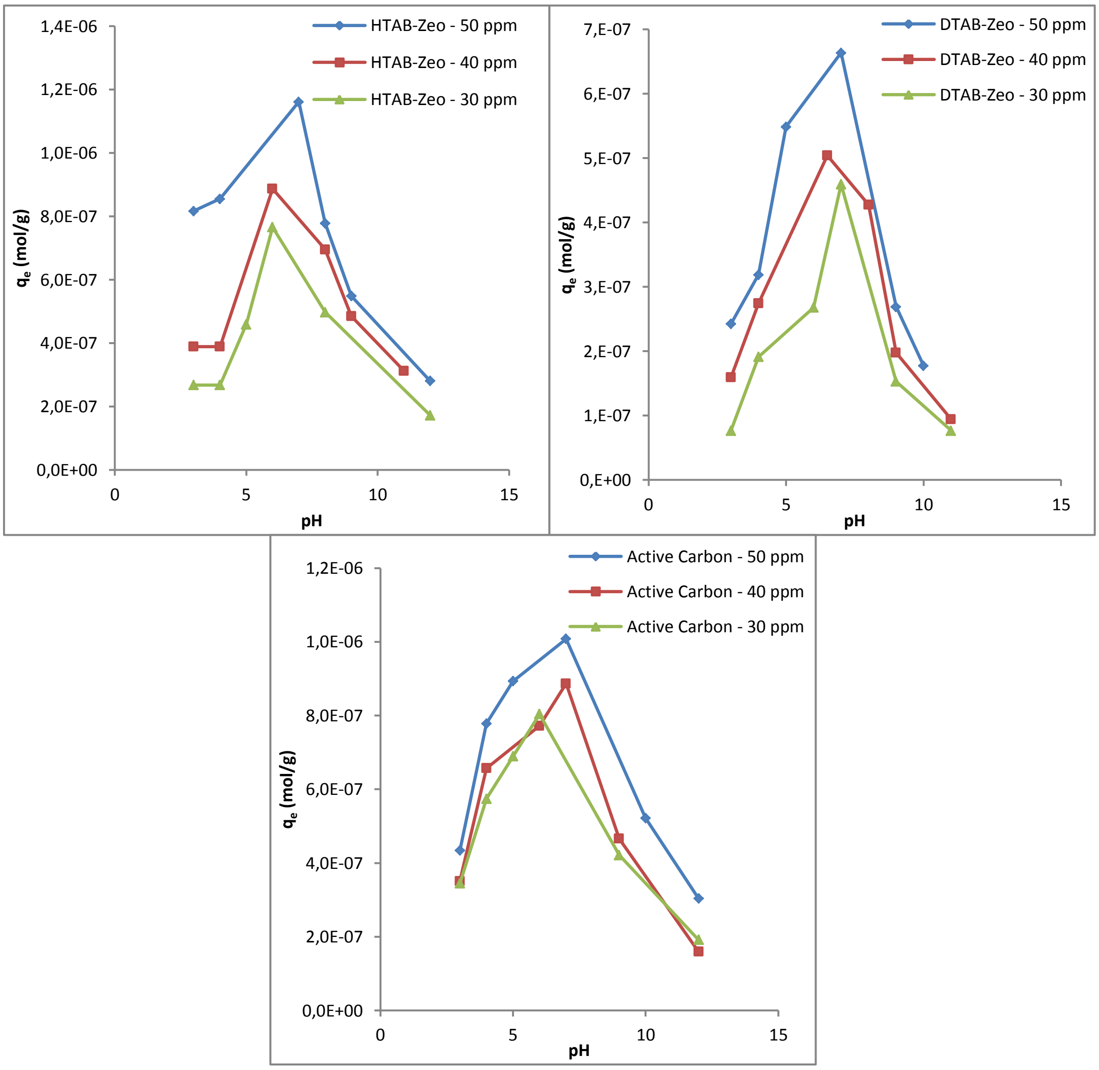


Figure 8.42 Effect of pH on Adsorption of Diazinon (App. Table C.58, C.59, C.60)

Adsorption of fenitrothion on adsorbents are shown in Figure 8.43. Fenitrothion degrades rapidly in low or high pH of solution. As it is seen from figures, minimum adsorption of fenitrohion was obtained at pH 3 and pH 11 and maximum fenitrothion was adsorbed at pH 7. Although adsorption capacity of activated carbon seem unaffected by pH of the solution, maximum fenitrothion adsorption was obtained at pH 7 at high initial concentration of fenitrothion. Therefore, pH value was chosen as neutral pH for fenitrothion adsorption.

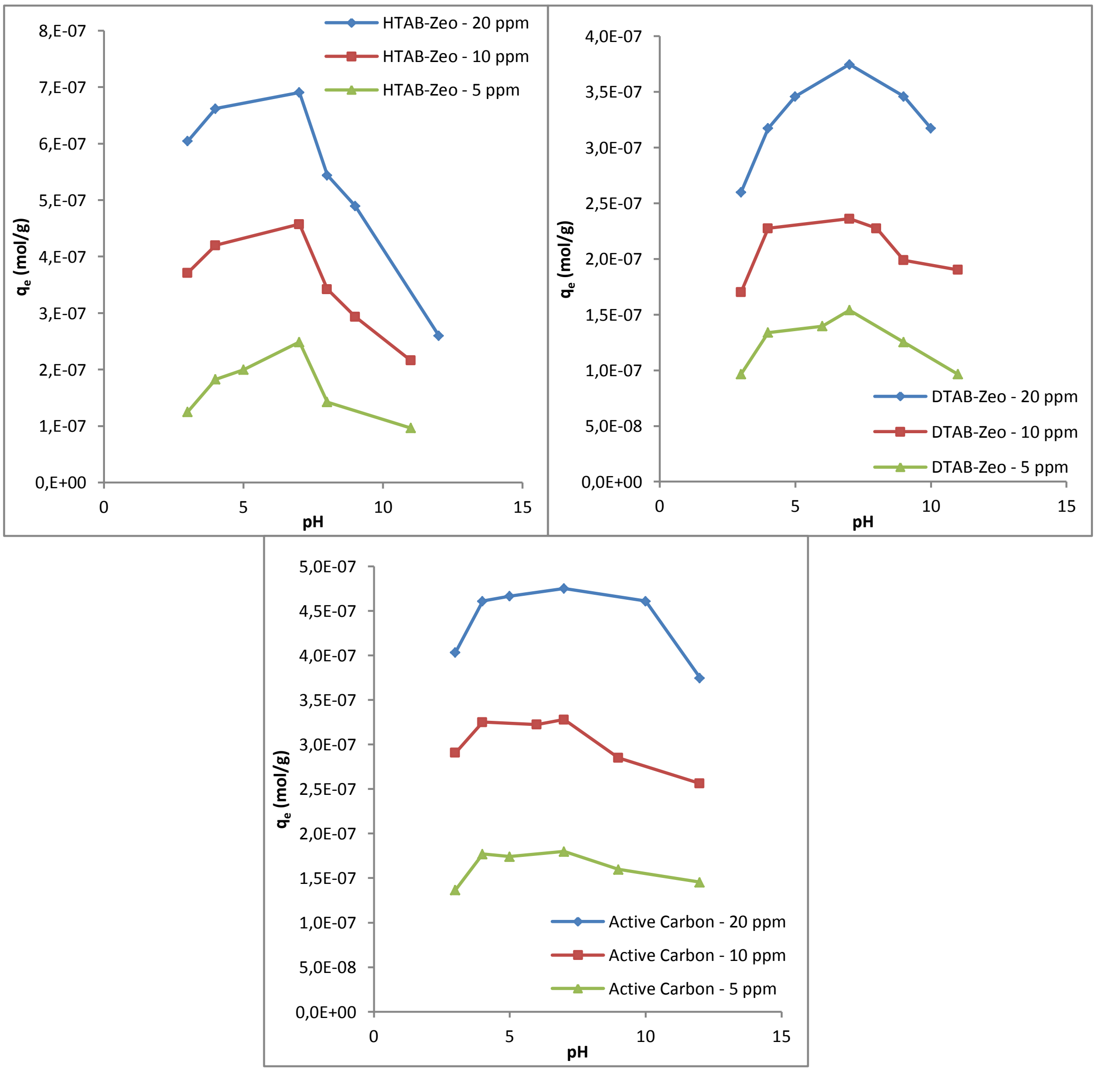


Figure 8.43 Effect of pH on Adsorption of Fenitrothion (App. Table C.82, C.83, C.84

Adsorption of trifluralin on adsorbents are shown in Figure 8.44. Adsorption of trifluralin on organo-zeolites and activated carbon was slightly affected by pH of solution at low initial concentration of pesticide. However, at high initial concentration of pesticide, the maximum amount of adsorbed trifluralin was obtained at pH 7 on each of three adsorbents. As it is seen from figures, adsorption capacities of adsorbents are decreased with increased pH of solution.

Therefore, pH value was chosen as neutral pH for trifluralin adsorption.

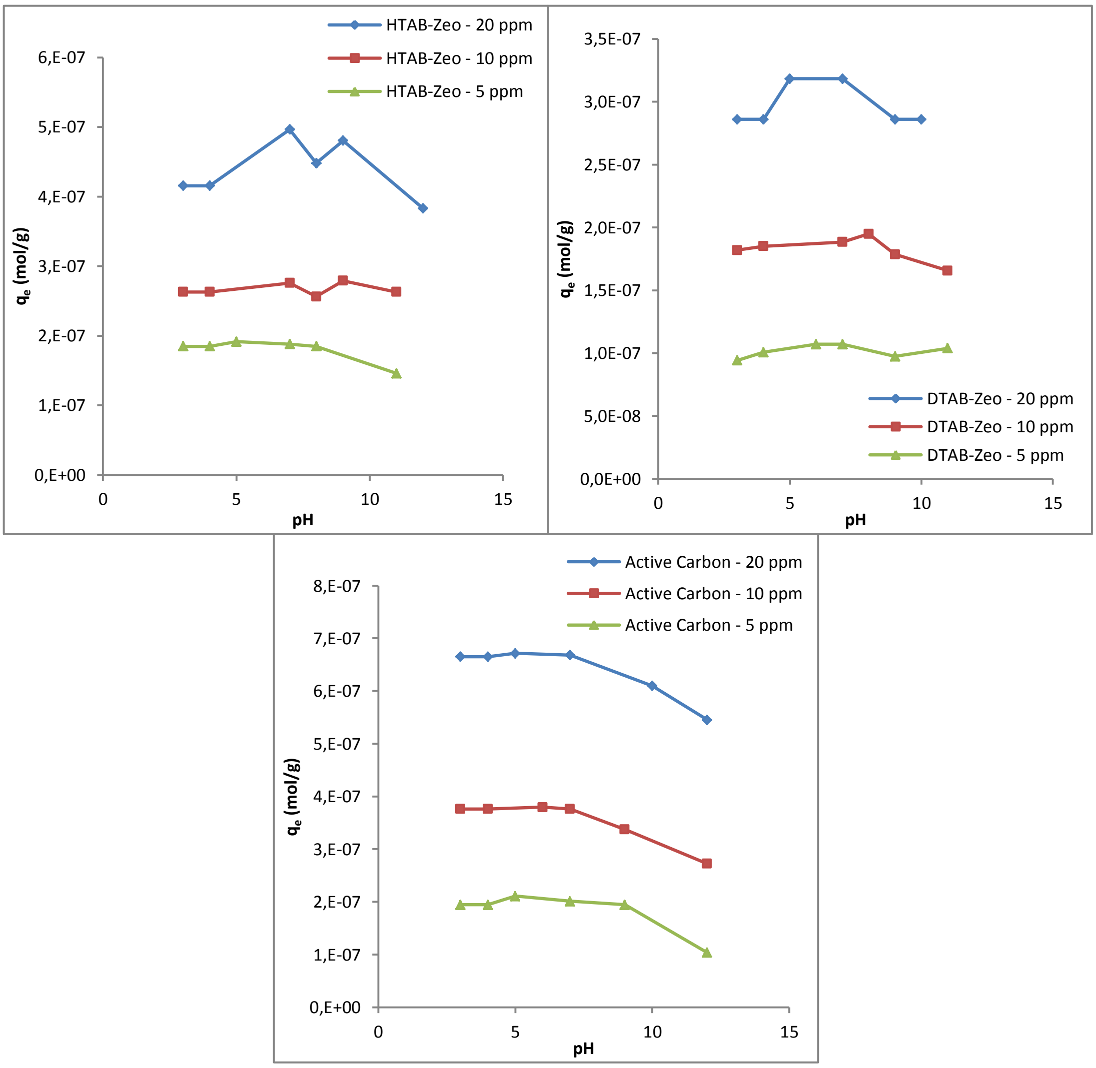


Figure 8.44 Effect of pH on Adsorption of Trifluralin (App. Table C.106, C.107, C.108)

8.4.4 Adsorption Isotherms of Pesticides

Two isotherms (Langmuir, and Freundlich) were used to describe the equilibrium between adsorbed pesticide on the adsorbent (q_e) and pesticide in solution (C_e) at different temperatures.

Langmuir adsorption model is predicated on the assumptions that adsorption energy is constant and independent of surface coverage; that adsorption occurs on localized sites with no interaction between adsorbate molecules, and that maximum adsorption occurs when the surface is covered by a monolayer adsorbate (Langmuir, 1918).

In order to determine the Langmuir constants, q_{max} and K_L, Eq. (8) was used. Langmuir constant, q_{max}, represents the monolayer saturation at equilibrium. The other mono component Langmuir constant K_L, indicates the affinity for the binding of pesticide on adsorbents. A high K_L value indicates a high affinity. Linear plots of C_e/q_e versus C_e were employed to determine the value of q_{max} (mol/g) and K_L (lt/mg).

Freundlich isotherm equation is based on the assumption that surface is heterogeneous and consisting of sites with different adsorption potentials, and each type of sites is assumed to adsorb molecules, as in the Langmuir equation (Perry & Green, 1999).

In order to determine the Freundlich constants, n and K_F, Eq. (10) was used. Freundlich constant, n, is related to intensity of adsorption. If the value of n is in the range $1< n <10$, the adsorption is favorable. Another Freundlich constant, K_F, has been used as a relative measure of adsorption capacity. Linear plots of ln q_e versus ln C_e employed to determine value of Freundlich constants (n and K_F).

Langmuir and Freundlich adsorption isotherms of 2,4-D on three adsorbents are shown in Figure 8.45, and results are tabulated in Table 8.20. As it is seen from the table higher K_L ($6.56 \times 10^{+3}$ lt/mol) value was obtained at 55° C with activated carbon. A higher value of K_L implied strong bonding of 2,4-D to activated carbon at this temperature.

The q_{max} value is increased with increasing temperature for activated carbon while is decreased for organo-zeolites. From Table 8.20, Langmuir isotherm exhibits higher correlation coefficient values (R^2), which is considerably better fit compared to Freundlich isotherm.

According to these results, it can be said that the adsorption of 2,4-D is monolayer on three adsorbents at different temperatures. Decreasing in adsorption capacities of organo-zeolites may be due to decreasing of ion exchange capacity of cationic surfactants with increasing temperature.

Table 8.20 Adsorption Isotherm Parameters of 2,4-D on Adsorbents

	Temperature	Langmuir Isotherm			Freundlich Isotherm		
	(°C)	q_{max} (mol/g)	K_L (lt/mol)	R^2	n	K_F	R^2
HTAB – Zeo	25	2.92×10^{-5}	$3.12 \times 10^{+3}$	0.9695	2.976	2.26×10^{-4}	0.9536
	35	2.89×10^{-5}	$1.97 \times 10^{+3}$	0.9542	2.225	4.32×10^{-4}	0.8782
	55	2.82×10^{-5}	$1.01 \times 10^{+3}$	0.9961	1.848	5.90×10^{-4}	0.9898
DTAB – Zeo	25	1.47×10^{-5}	$8.98 \times 10^{+2}$	0.9632	1.954	2.36×10^{-4}	0,9444
	35	1.40×10^{-5}	$5.98 \times 10^{+2}$	0.9999	1.727	2.84×10^{-4}	0.9980
	55	1.38×10^{-5}	$3.20 \times 10^{+2}$	0.9870	1.411	4.45×10^{-4}	0.9947
Activated Carbon	25	2.71×10^{-5}	$5.63 \times 10^{+3}$	0.9758	3.436	1.79×10^{-4}	0.7411
	35	3.15×10^{-5}	$5.79 \times 10^{+3}$	0.9907	3.170	2.54×10^{-4}	0.8844
	55	3.51×10^{-5}	$6.56 \times 10^{+3}$	0.9893	3.307	2.64×10^{-4}	0.9902

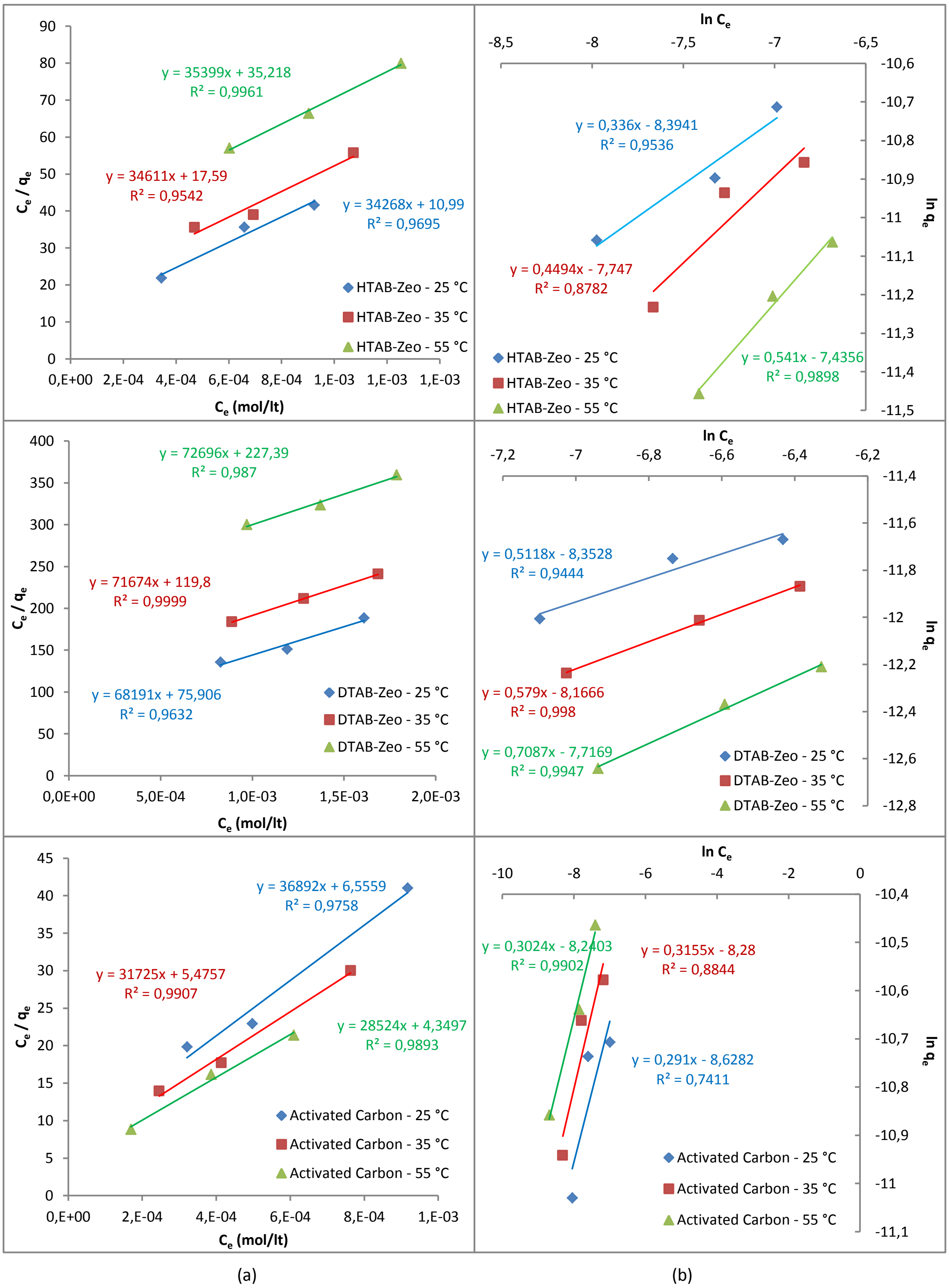


Figure 8.45 Adsorption Isotherms of 2,4-D on Adsorbents (App. Table C.13, C.14, C.15, C.16, C.17, C.18). (a) Langmuir Isotherm, (b) Freundlich Isotherm

Langmuir and Freundlich adsorption isotherms of propanil on three adsorbents are shown in Figure 8.46, and results are tabulated in Table 8.21. As it is seen from the table, higher K_L values were obtained as 4.61 x 10^{+4} at 55° C for HTAB-Zeolite, 1.02 x 10^{+4} at 55° C for and DTAB-Zeolite, and 3.72 x 10^{+4} lt/mol at 55° C for activated carbon. Within the obtained K_L values, it can be said that there is a strong bonding between HTAB-Zeolite surface and propanil at 55° C. The q_{max} value is increased with increasing temperature for organo-zeolites and activated carbon. From Table 8.21, Langmuir isotherm exhibits higher correlation coefficient values (R^2) for DTAB-Zeolite, which is considerably better fit compared with Freundlich isotherm. The adsorption data obtained from HTAB-Zeolite and activated carbon fit well to both Langmuir and Freundlich isotherm, which means that adsorption of propanil on HTAB-Zeolite and activated carbon was occured by chemisorption and physisorption at all temperatures.

The adsorption of propanil was found as monolayer on DTAB-Zeolite and multilayer on HTAB-Zeolite and activated carbon. This is due to preferential adsorption of propanil molecules by more hydrophobic surfaces..

Table 8.21 Adsorption Isotherm Parameters of Propanil on Adsorbents

	Temperature (°C)	Langmuir Isotherm			Freundlich Isotherm		
		q_{max} (mol/g)	K_L (lt/mol)	R^2	n	K_F	R^2
HTAB – Zeo	25	6.58 x 10^{-6}	1.54 x 10^{+4}	0.9999	3.014	8.42 x 10^{-5}	0.9897
	35	8.99 x 10^{-6}	2.48 x 10^{+4}	0.9841	2.869	1.57 x 10^{-4}	0.9849
	55	1.04 x 10^{-5}	4.61 x 10^{+4}	0.9865	2.745	2.64 x 10^{-4}	0.9924
DTAB – Zeo	25	4.42 x 10^{-6}	4.38 x 10^{+3}	0.9811	2.008	1.43 x 10^{-4}	0.9657
	35	5.09 x 10^{-6}	8.33 x 10^{+3}	0.9808	2.520	9.25 x 10^{-5}	0.9242
	55	6.48 x 10^{-6}	1.02 x 10^{+4}	0.9893	2.660	1.06 x 10^{-4}	0.9909
Activated Carbon	25	9.46 x 10^{-6}	1.03 x 10^{+4}	0.9727	2.060	4.14 x 10^{-4}	0.9384
	35	1.01 x 10^{-5}	1.97 x 10^{+4}	0.9954	2.383	3.18 x 10^{-4}	0.9998
	55	1.22 x 10^{-5}	3.72 x 10^{+4}	0.993	2.161	7.83 x 10^{-4}	0.9664

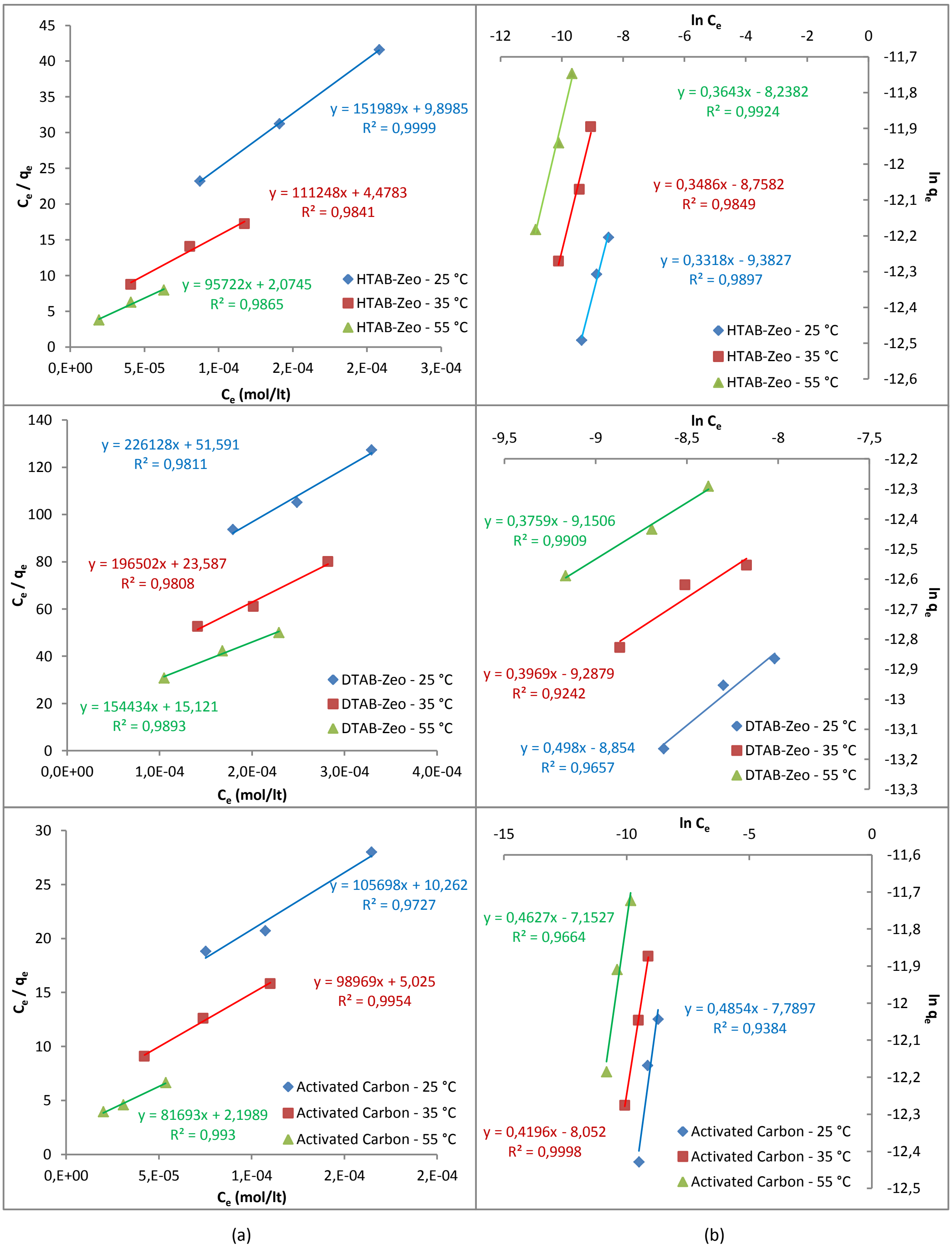


Figure 8.46 Adsorption Isotherms of Propanil on Adsorbents (App. Table C.37, C.38, C.39, C.40, C.41, C.42). (a) Langmuir Isotherm, (b) Freundlich Isotherm

Langmuir and Freundlich adsorption isotherms of diazinon on three adsorbents are shown in Figure 8.47, and results are tabulated in Table 8.22. As it is seen from the table higher K_L value was obtained as 1.82 x 10^{+4} lt/mol at 25° C with activated carbon. The q_{max} value is decreased with increasing temperature for organo-zeolites and activated carbon. From Table 8.22, Freundlich isotherm exhibits higher correlation coefficient values (R^2) for three of adsorbents, which is considerably better fit compared with Langmuir isotherm. From the data obtained from adsorption experiments, it can be seen that adsorption of diazinon on organo-zeolites and activated carbon was governed by physisorption at all temperatures.

Table 8.22 Adsorption Isotherm Parameters of Diazinon on Adsorbents

	Temperature	Langmuir Isotherm			Freundlich Isotherm		
	(°C)	q_{max} (mol/g)	K_L (lt/mol)	R^2	n	K_F	R^2
HTAB – Zeo	25	9.77 x 10^{-6}	4.07 x 10^{+3}	0.8737	1.188	6.86 x 10^{-3}	0.9922
	35	3.00 x 10^{-6}	5.19 x 10^{+3}	0.9936	1.423	6.61 x 10^{-4}	0.9966
	45	2.92 x 10^{-6}	1.92 x 10^{+3}	0.8859	1.191	1.07 x 10^{-3}	0.9930
DTAB – Zeo	25	2.23 x 10^{-6}	8.77 x 10^{+3}	0.9746	1.684	2.47 x 10^{-4}	0.9781
	35	1.14 x 10^{-6}	9.84 x 10^{+3}	0.8564	2.089	4.62 x 10^{-5}	0.8844
	45	1.12 x 10^{-6}	3.82 x 10^{+3}	0.9181	1.402	2.20 x 10^{-4}	0.9787
Activated Carbon	25	4.74 x 10^{-6}	1.82 x 10^{+4}	0.9997	1.643	9.41 x 10^{-4}	0.9975
	35	2.58 x 10^{-6}	1.35 x 10^{+4}	0.8827	1.975	1.58 x 10^{-4}	0.9300
	45	2.47 x 10^{-6}	6.16 x 10^{+3}	0.9490	1.501	4.34 x 10^{-4}	0.9782

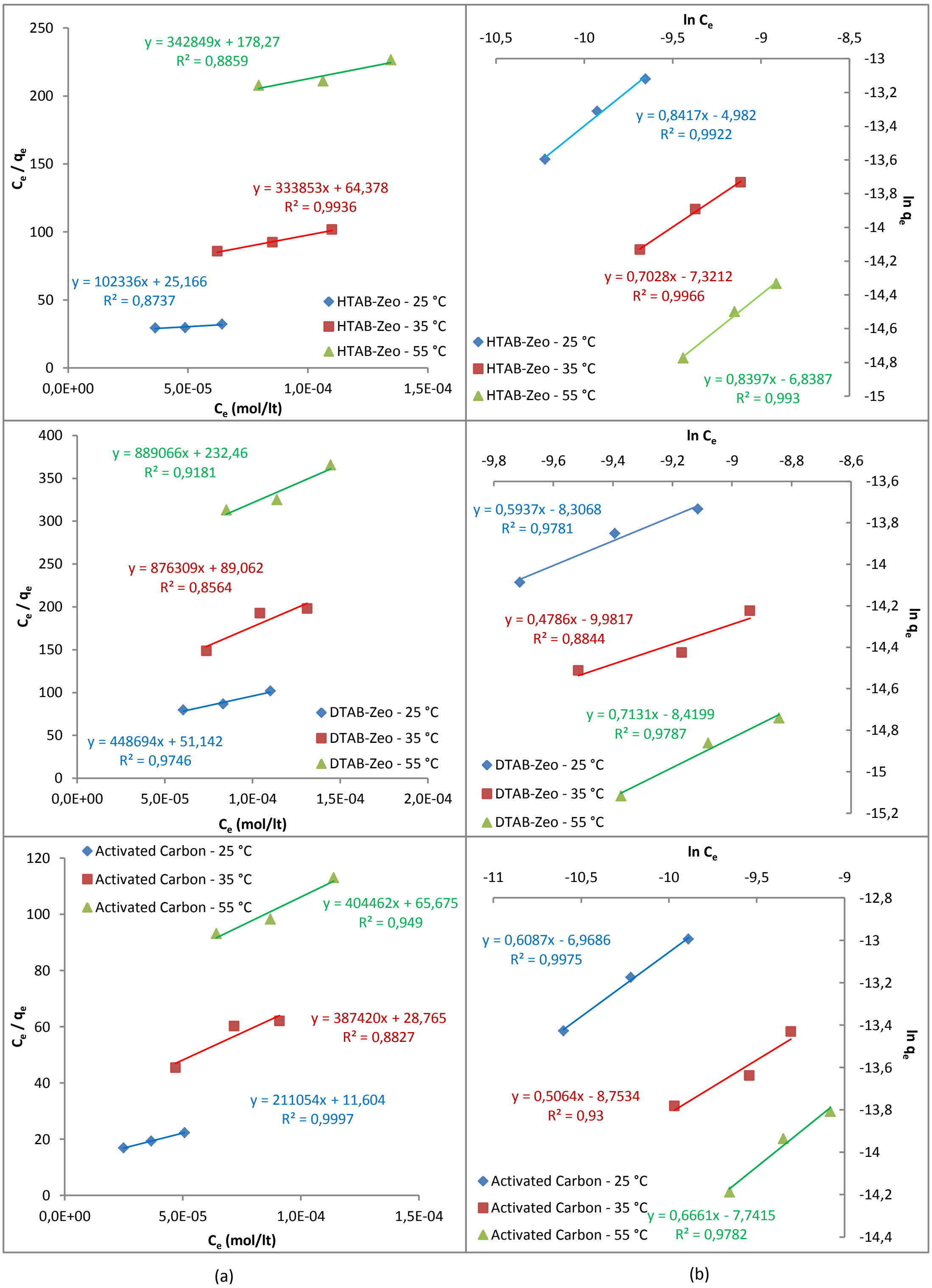


Figure 8.47 Adsorption Isotherms of Diazinon on Adsorbents (App. Table C.61, C.62, C.63, C.64, C.65, C.66). (a) Langmuir Isotherm, (b) Freundlich Isotherm

Langmuir and Freundlich adsorption isotherms of fenitrothion on three adsorbents are shown in Figure 8.48, and results are tabulated in Table 8.23. As it is seen from the table higher K_L value was obtained as $4.24 \times 10^{+4}$ lt/mol at 25° C with HTAB-Zeolite. The q_{max} value is decreased with increasing temperature for organo-zeolites and activated carbon. From Table 8.23, Freundlich isotherm exhibits higher correlation coefficient values (R^2) for three of adsorbents, which is considerably better fit compared with Langmuir isotherm.

From the data obtained with adsorption experiments, it can be seen that adsorption of fenitrothion on organo-zeolites and activated carbon was governed by physisorption at all temperatures.

Table 8.23 Adsorption Isotherm Parameters of Fenitrothion on Adsorbents

	Temperature	Langmuir Isotherm			Freundlich Isotherm		
	(°C)	q_{max} (mol/g)	K_L (lt/mol)	R^2	n	K_F	R^2
HTAB – Zeo	25	1.66×10^{-6}	$4.24 \times 10^{+4}$	0.9999	1.501	1×10^{-3}	0.9922
	35	1.32×10^{-6}	$1.76 \times 10^{+4}$	0.977	1.347	1.01×10^{-3}	0.9859
	45	1.07×10^{-6}	$1.41 \times 10^{+4}$	0.9801	1.365	6.34×10^{-4}	1
DTAB – Zeo	25	1.67×10^{-6}	$1.47 \times 10^{+4}$	0.9211	1.323	1.30×10^{-3}	0.9984
	35	1.55×10^{-6}	$8.575 \times 10^{+3}$	0.9979	1.217	1.62×10^{-3}	0.9993
	45	1.54×10^{-6}	$5.811 \times 10^{+3}$	0.6683	1.196	1.36×10^{-3}	0.9923
Activated Carbon	25	2.65×10^{-6}	$3.06 \times 10^{+4}$	0.9295	1.321	3.63×10^{-3}	0.9991
	35	2.26×10^{-6}	$9.35 \times 10^{+3}$	0.811	1.221	2.45×10^{-3}	0.9963
	45	1.67×10^{-6}	$9.67 \times 10^{+3}$	0.9852	1.234	1.64×10^{-3}	0.9999

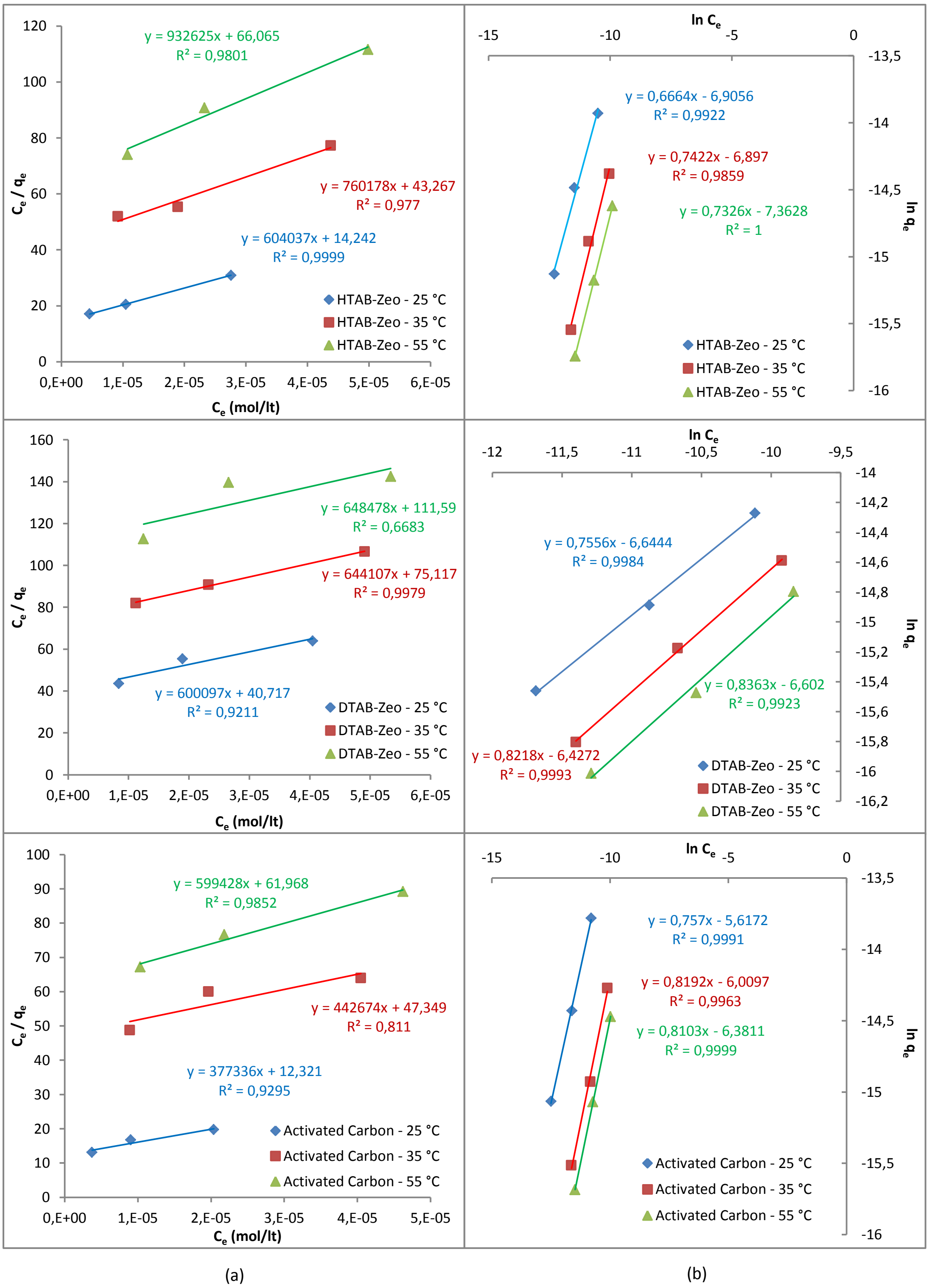


Figure 8.48 Adsorption Isotherms of Fenitrothion on Adsorbents (App. Table C.85, C.86, C.87, C.88, C.89, C.90). (a) Langmuir Isotherm, (b) Freundlich Isotherm

Langmuir and Freundlich adsorption isotherms of trifluralin on three adsorbents are shown in Figure 8.49, and results are tabulated in Table 8.24. As it is seen from the table higher K_L value was obtained as 5.07 x 10^{+5} lt/mol at 55° C with HTAB-Zeolite. The q_{max} value is increased with increasing temperature for organo-zeolites and activated carbon. From Table 8.24, Freundlich isotherm exhibits higher correlation coefficient values (R^2) for three of adsorbents, which is considerably better fit compared with Langmuir isotherm. From the data obtained from adsorption experiments, it can be seen that adsorption of trifluralin on organo-zeolites and activated carbon was governed by physisorption at all temperatures.

Table 8.24 Adsorption Isotherm Parameters of Trifluralin on Adsorbents

	Temperature (°C)	Langmuir Isotherm			Freundlich Isotherm		
		q_{max} (mol/g)	K_L (lt/mol)	R^2	n	K_F	R^2
HTAB – Zeo	25	1.29 x 10^{-6}	2 x 10^{+5}	0.9734	1.965	2.90 x 10^{-4}	0.9996
	35	1.32 x 10^{-6}	2.98 x 10^{+5}	0.9251	2.154	2.05 x 10^{-4}	0.9848
	45	1.32 x 10^{-6}	5.07 x 10^{+5}	0.8963	2.389	1.45 x 10^{-4}	0.9678
DTAB – Zeo	25	1.52 x 10^{-6}	2.27 x 10^{+4}	0.9884	1.33	1.59 x 10^{-3}	0.9997
	35	1.65 x 10^{-6}	2.30 x 10^{+4}	0.9935	1.31	1.95 x 10^{-3}	0.9993
	45	1.68 x 10^{-6}	3.27 x 10^{+4}	0.9936	1.35	1.94 x 10^{-3}	0.9973
Activated Carbon	25	2.04 x 10^{-6}	7.99 x 10^{+4}	0.9865	1.406	3.24 x 10^{-3}	0.9996
	35	2.05 x 10^{-6}	1.24 x 10^{+5}	0.9882	1.414	4.21 x 10^{-3}	0.9839
	45	2.12 x 10^{-6}	1.80 x 10^{+5}	0.9815	1.450	4.51 x 10^{-3}	0.9998

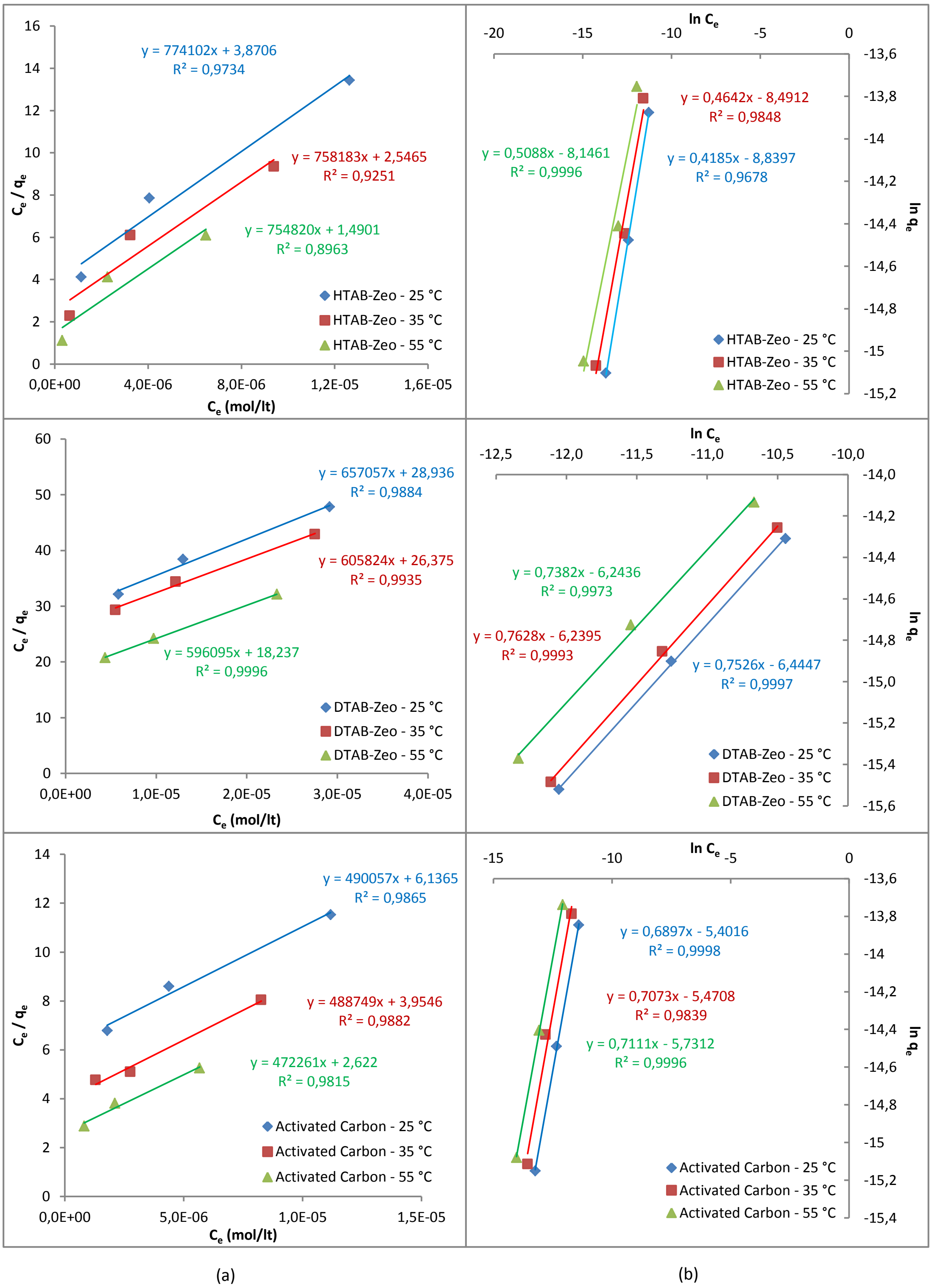


Figure 8.49 Adsorption Isotherms of Trifluralin on Adsorbents (App. Table C.109, C.110, C.111, C.112, C.113, C.114). (a) Langmuir Isotherm, (b) Freundlich Isotherm

8.4.5 Kinetic Parameters of Pesticide Adsorption

The modeling of the kinetic of pesticide adsorption on organo-zeolites and activated carbon was investigated by two common models, namely, the Lagergren pseudo first order model (Eq. 15) and pseudo second order model (Eq. 16).

Kinetic models for adsorption of 2,4-D on adsorbents are shown in Figure 8.50, and the coefficients of correlation as well as the kinetic parameters of pesticide adsorption on organo-zeolite and activated carbon are tabulated in Table 8.25.

From the given results, the correlation coefficient of the second order model for adsorption of 2,4-D on DTAB-Zeolite is low ($R^2 < 0.73$), and the calculated q_e values obtained from the first order kinetic model was not reasonable. However, the correlation coefficient of the second order model for adsorption on HTAB-Zeolite and activated carbon are greater than 0.97. The high value of the correlation coefficient for HTAB-Zeolite and activated carbon is good proof that the adsorption process follows the pseudo second order rate equation.

Table 8.25 Pseudo First Order and Pseudo Second Order Kinetics Parameters for Adsorption of 2,4-D

	Initial Concentration (mg/L)	Lagergren Pseudo First Order Kinetic			Pseudo Second Order Kinetic		
		k_1	qe (mol/g)	R^2	k_2	qe (mol/g)	R^2
HTAB – Zeo	450	48×10^{-4}	9.53×10^{-3}	0.8833	348.75	3.09×10^{-5}	0.9790
	350	32×10^{-4}	9.70×10^{-3}	0.8914	577.21	2.40×10^{-5}	0.9857
	250	23×10^{-4}	9.71×10^{-3}	0.8512	863.53	1.96×10^{-5}	0.9835
DTAB – Zeo	450	44×10^{-4}	7.82×10^{-3}	0.8953	259.70	1.96×10^{-5}	0.6248
	350	39×10^{-4}	7.83×10^{-3}	0.9118	400.43	1.58×10^{-5}	0.6452
	250	25×10^{-4}	7.75×10^{-3}	0.8904	814.45	1.11×10^{-5}	0.7253
Activated Carbon	450	41×10^{-4}	9.26×10^{-3}	0.9431	198.99	3.17×10^{-5}	0.9724
	350	37×10^{-4}	9.48×10^{-3}	0.9759	313.78	2.82×10^{-5}	0.9977
	250	18×10^{-4}	9.23×10^{-3}	0.8734	639.66	1.98×10^{-5}	0.9971

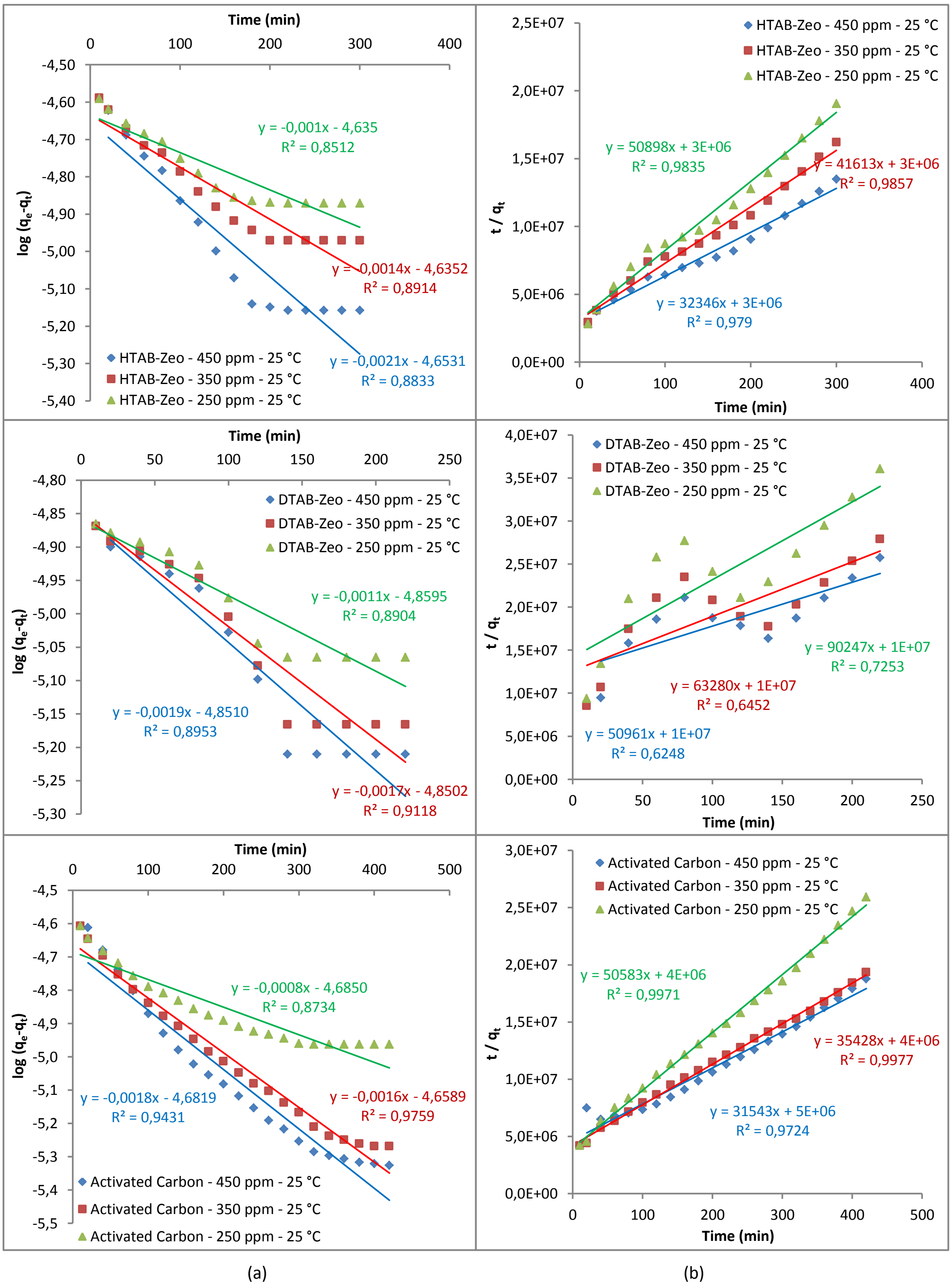


Figure 8.50 Kinetic Models for Adsorption of 2,4-D on Adsorbents (App. Table C.19, C.20, C.21, C.22, C.23, C.24). (a) Lagergren Pseudo First Order Kinetic Model, (b) Pseudo Second Order Kinetic Model

Kinetic models for adsorption of propanil on adsorbents are shown in Figure 8.51, and the coefficients of correlation as well as the kinetic parameters of pesticide adsorption on organo-zeolite and activated carbon are tabulated in Table 8.26.

As it is seen from the Table 8.26, the correlation coefficients of the pseudo first order model for adsorption on three adsorbents are low (R^2 < 0.98). Calculated q_e values obtained from the first order kinetic model was not sensible. However, the correlation coefficients of the second order model for adsorption on organo-zeolites and activated carbon are greater than 0.98. The high value of the correlation coefficient for organo-zeolites and activated carbon is good proof that the adsorption process follows the pseudo second order rate equation.

Table 8.26 Pseudo First Order and Pseudo Second Order Kinetics Parameters for Adsorption of Propanil

	Initial Concentration (mg/L)	Lagergren Pseudo First Order Kinetic			Pseudo Second Order Kinetic		
		k_1	qe (mol/g)	R^2	k_2	qe (mol/g)	R^2
HTAB – Zeo	100	41 x 10^{-4}	4.17 x 10^{-3}	0.8071	81.34 x 10^{+2}	5.54 x 10^{-6}	0.9991
	80	39 x 10^{-4}	4.56 x 10^{-3}	0.8221	98.20 x 10^{+2}	5.05 x 10^{-6}	0.9984
	60	23 x 10^{-4}	4.61 x 10^{-3}	0.7001	150.39 x 10^{+2}	4.08 x 10^{-6}	0.9983
DTAB – Zeo	100	37 x 10^{-4}	4.39 x 10^{-3}	0.9452	21.71 x 10^{+2}	3.92 x 10^{-6}	0.9911
	80	35 x 10^{-4}	4.43 x 10^{-3}	0.9177	43.05 x 10^{+2}	3.41 x 10^{-6}	0.9856
	60	23 x 10^{-4}	4.42 x 10^{-3}	0.8647	75.17 x 10^{+2}	2.58 x 10^{-6}	0.9898
Activated Carbon	100	16 x 10^{-4}	5.47 x 10^{-3}	0.8365	28.74 x 10^{+2}	6.59 x 10^{-6}	0.9989
	80	14 x 10^{-4}	5.65 x 10^{-3}	0.7777	43.24 x 10^{+2}	5.75 x 10^{-6}	0.9977
	60	7 x 10^{-4}	5.76 x 10^{-3}	0.6991	89.83 x 10^{+2}	4.31 x 10^{-6}	0.9991

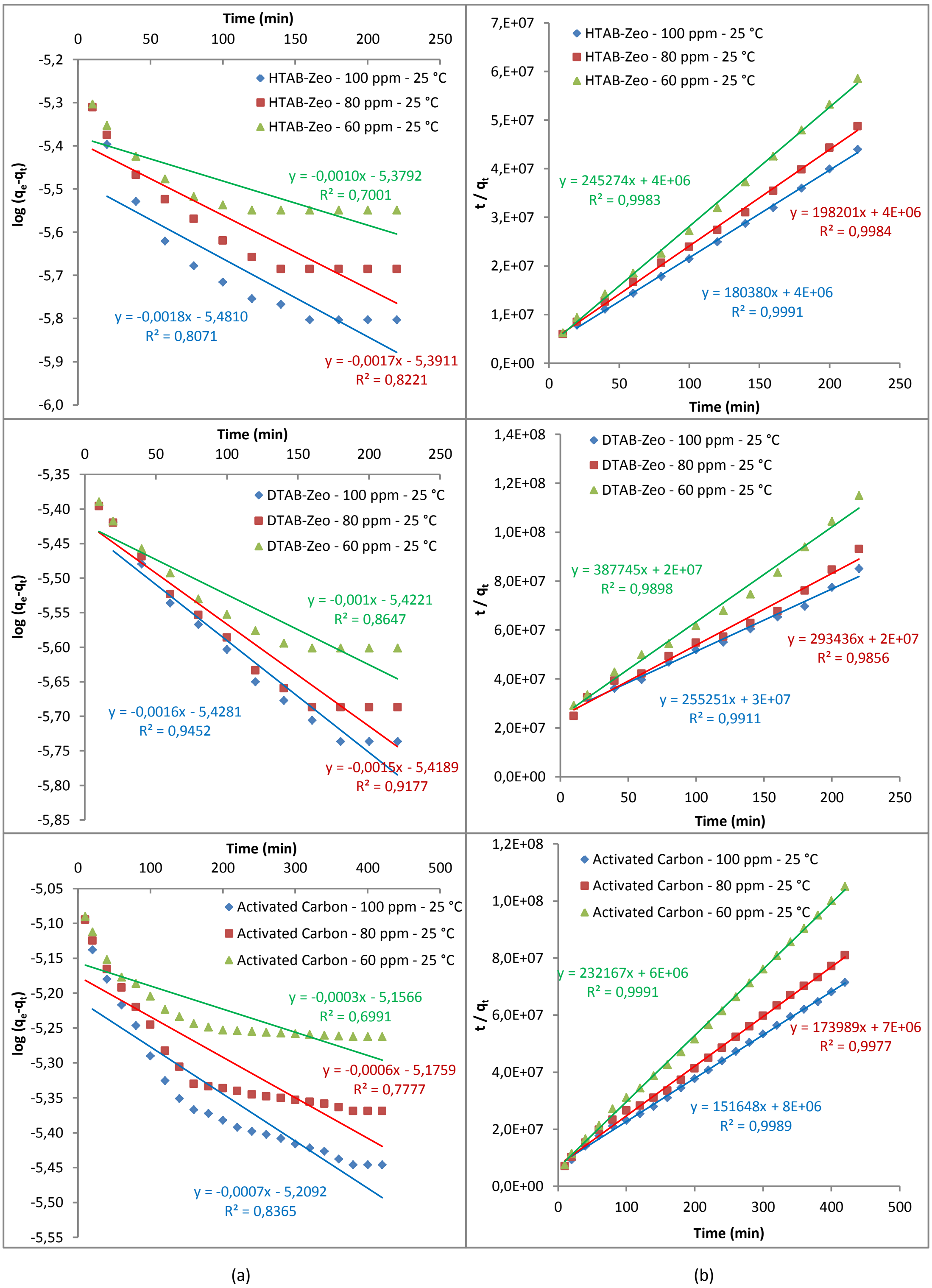


Figure 8.51 Kinetic Models for Adsorption of Propanil on Adsorbents (App. Table C.43, C.44, C.45, C.46, C.47, C.48). (a) Lagergren Pseudo First Order Kinetic Model, (b) Pseudo Second Order Kinetic Model

Kinetic models for adsorption of diazinon on adsorbents are shown in Figure 8.52, and the coefficients of correlation as well as the kinetic parameters of pesticide adsorption on organo-zeolite and activated carbon are tabulated in Table 8.27.

From the given results, the correlation coefficients of the pseudo first order model for adsorption on three adsorbents are low ($R^2 < 0.97$), however, the correlation coefficients of the second order model for adsorption on organo-zeolites and activated carbon are greater than 0.97. Calculated q_e values obtained from the second order kinetic model was more reasonable than q_e values obtained from first order kinetic model. The high value of the correlation coefficient for organo-zeolites and activated carbon is good proof that the adsorption process follows the pseudo second order rate equation.

Table 8.27 Pseudo First Order and Pseudo Second Order Kinetics Parameters for Adsorption of Diazinon

	Initial Concentration (mg/L)	Lagergren Pseudo First Order Kinetic			Pseudo Second Order Kinetic		
		k_1	qe (mol/g)	R^2	k_2	qe (mol/g)	R^2
HTAB – Zeo	50	8×10^{-4}	6.46×10^{-3}	0.9513	$45 \times 10^{+2}$	2.72×10^{-6}	0.978
	40	7×10^{-4}	6.50×10^{-3}	0.9269	$76.72 \times 10^{+2}$	2.08×10^{-6}	0.983
	30	4×10^{-4}	6.50×10^{-3}	0.8964	$233.80 \times 10^{+2}$	1.46×10^{-6}	0.989
DTAB – Zeo	50	23×10^{-4}	3.22×10^{-3}	0.9851	$113.36 \times 10^{+2}$	1.33×10^{-6}	0.965
	40	20×10^{-4}	3.27×10^{-3}	0.9595	$189.23 \times 10^{+2}$	1.15×10^{-6}	0.973
	30	14×10^{-4}	3.28×10^{-3}	0.9291	$250 \times 10^{+2}$	1×10^{-6}	0.988
Activated Carbon	50	13×10^{-4}	4.46×10^{-3}	0.9083	$29.54 \times 10^{+2}$	2.91×10^{-6}	0.992
	40	10×10^{-4}	4.52×10^{-3}	0.8531	$61.43 \times 10^{+2}$	2.33×10^{-6}	0.993
	30	7×10^{-4}	4.56×10^{-3}	0.8109	$82.35 \times 10^{+2}$	1.74×10^{-6}	0.997

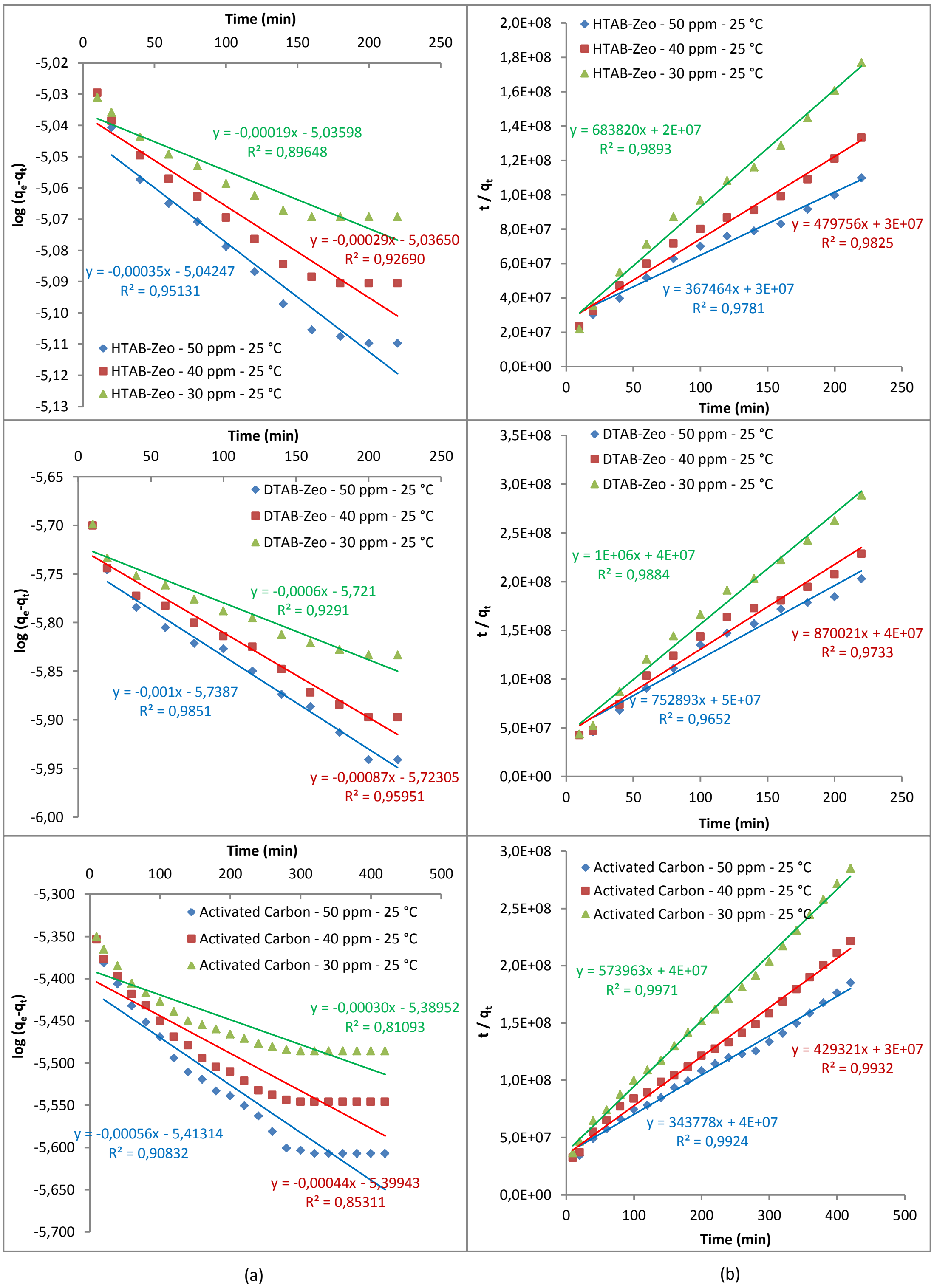


Figure 8.52 Kinetic Models for Adsorption of Diazinon on Adsorbents (App. Table C.67, C.68, C.69, C.70, C.71, C.72). (a) Lagergren Pseudo First Order Kinetic Model, (b) Pseudo Second Order Kinetic Model

Kinetic models for adsorption of fenitrothion on adsorbents are shown in Figure 8.53, and the coefficients of correlation as well as the kinetic parameters of pesticide adsorption on organo-zeolite and activated carbon are tabulated in Table 8.28.

From the given results, the correlation coefficients of the pseudo second order model for adsorption on three adsorbents are greater than 0.97, however, that of pseudo first order model are low ($R^2 < 0.90$). Calculated q_e values obtained from the second order kinetic model was more reasonable. The high value of the correlation coefficient for organo-zeolites and activated carbon is good proof that the adsorption process follows the pseudo second order rate equation.

Table 8.28 Pseudo First Order and Pseudo Second Order Kinetics Parameters for Adsorption of Fenitrothion

	Initial Concentration (mg/L)	Lagergren Pseudo First Order Kinetic			Pseudo Second Order Kinetic		
		k_1	qe (mol/g)	R^2	k_2	qe (mol/g)	R^2
HTAB – Zeo	20	17×10^{-4}	2.51×10^{-3}	0.7198	$5 \times 10^{+4}$	1×10^{-6}	0.9981
	10	7.8×10^{-4}	2.78×10^{-3}	0.6651	$20 \times 10^{+4}$	5×10^{-7}	0.9987
	5	2.5×10^{-4}	2.91×10^{-3}	0.6013	$80 \times 10^{+4}$	2.50×10^{-7}	0.9996
DTAB – Zeo	20	18×10^{-4}	2.93×10^{-3}	0.8339	$9.22 \times 10^{+3}$	1.04×10^{-6}	0.908
	10	9×10^{-4}	2.99×10^{-3}	0.7804	$4 \times 10^{+4}$	5.10×10^{-7}	0.9778
	5	5×10^{-4}	3.02×10^{-3}	0.6688	$8 \times 10^{+4}$	2.50×10^{-7}	0.9819
Activated Carbon	20	9×10^{-4}	3.50×10^{-3}	0.8898	$8.48 \times 10^{+3}$	1.30×10^{-6}	0.9862
	10	3×10^{-4}	3.60×10^{-3}	0.7890	$5 \times 10^{+4}$	5×10^{-7}	0.9974
	5	1×10^{-4}	3.68×10^{-3}	0.8574	$9 \times 10^{+4}$	3.33×10^{-7}	0.9946

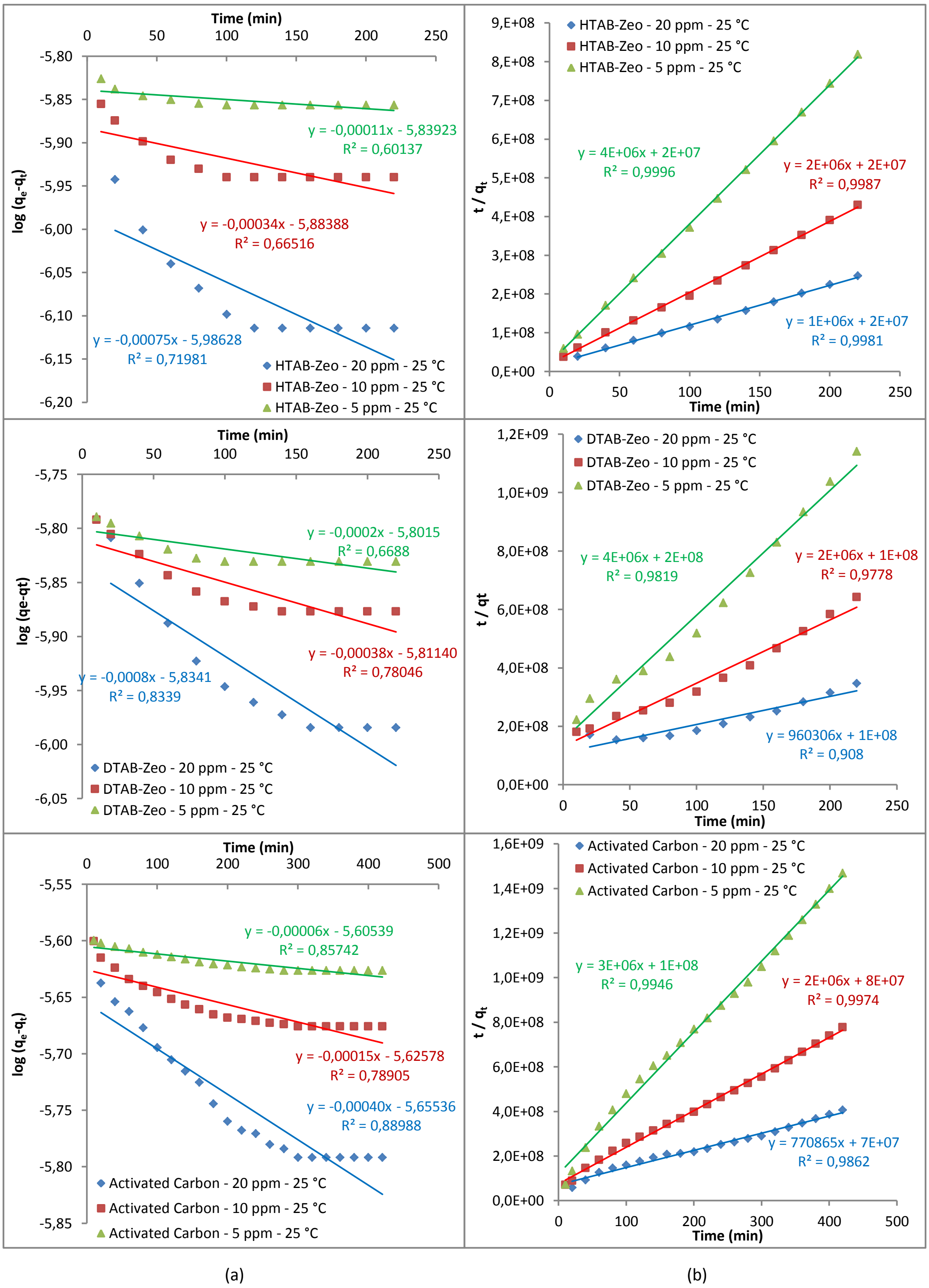


Figure 8.53 Kinetic Models for Adsorption of Fenitrothion on Adsorbents (App. Table C.91, C.92, C.93, C.94, C.95, C.96). (a) Lagergren Pseudo First Order Kinetic Model, (b) Pseudo Second Order Kinetic Model

Kinetic models for adsorption of trifluralin on adsorbents are shown in Figure 8.54, and the coefficients of correlation as well as the kinetic parameters of pesticide adsorption on organo-zeolite and activated carbon are tabulated in Table 8.29.

From the given results, the correlation coefficients of the pseudo first order model for adsorption on three adsorbents are low (R^2 < 0.90), and the calculated q_e values obtained from the first order kinetic model was not reasonable. However, the correlation coefficients of the second order model for adsorption on organo-zeolites and activated carbon are greater than 0.94. The high value of the correlation coefficient for organo-zeolites and activated carbon is good proof that the adsorption process follows the pseudo second order rate equation.

Table 8.29 Pseudo First Order and Pseudo Second Order Kinetics Parameters for Adsorption of Trifluralin

	Initial Concentration (mg/L)	Lagergren Pseudo First Order Kinetic			Pseudo Second Order Kinetic		
		k_1	qe (mol/g)	R^2	k_2	qe (mol/g)	R^2
HTAB – Zeo	20	53×10^{-4}	2.40×10^{-3}	0.8743	$13 \times 10^{+3}$	1.24×10^{-6}	0.953
	10	71×10^{-4}	2.37×10^{-3}	0.1012	$66.6 \times 10^{+3}$	5×10^{-7}	0.943
	5	16×10^{-4}	2.54×10^{-3}	0.0354	$15 \times 10^{+4}$	3.33×10^{-7}	0.983
DTAB – Zeo	20	21×10^{-4}	2.80×10^{-3}	0.9211	$10 \times 10^{+3}$	1×10^{-6}	0.956
	10	9×10^{-4}	2.88×10^{-3}	0.9209	$40 \times 10^{+3}$	5×10^{-7}	0.970
	5	5×10^{-4}	2.91×10^{-3}	0.9155	$12.5 \times 10^{+4}$	2×10^{-7}	0.981
Activated Carbon	20	8.52×10^{-4}	2.88×10^{-3}	0.7707	$29.5 \times 10^{+3}$	1×10^{-6}	0.999
	10	3.36×10^{-4}	3.13×10^{-3}	0.7591	$80 \times 10^{+3}$	5×10^{-7}	0.999
	5	1.31×10^{-4}	3.24×10^{-3}	0.7368	$22.8 \times 10^{+4}$	2.50×10^{-7}	0.999

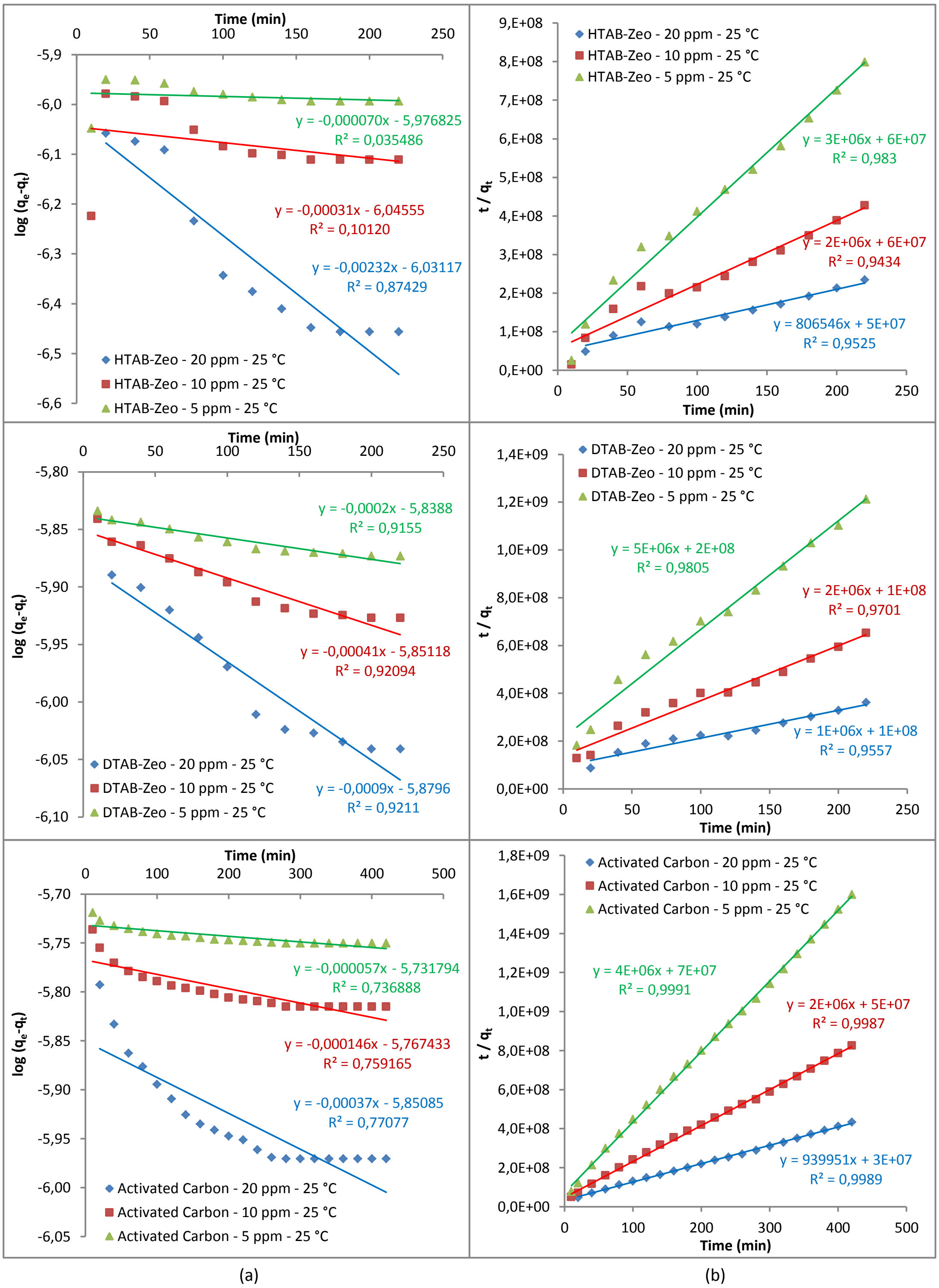


Figure 8.54 Kinetic Models for Adsorption of Trifluralin on Adsorbents (App. Table C.115, C.116, C.117, C.118, C.119, C.120). (a) Lagergren Pseudo First Order Kinetic Model, (b) Pseudo Second Order Kinetic Model

8.4.6 Thermodynamics Parameters of Pesticide Adsorption

In order to explain the effect of temperature on the adsorption mechanism, thermodynamic parameters were calculated by using the values of binding Langmuir constant, K_L. The activation energies were calculated from linearized Arrhenius equation (Eq. 17). A plot of ln k against the reciprocal of absolute temperature, 1/T, give the straight line. From the slope and y-intercept of plot, enthalpy change (ΔH°) and entropy change (ΔS) were calculated.

Calculated activation energies for 2,4-D adsorption on organo-zeolites and activated carbon are given in Table 8.30.

Table 8.30 Thermodynamic Parameters for Adsorption of 2,4-D

HTAB – Zeolite							
Tem. (K°)	K_L	ln K_L	1/T	ΔH (kJ/mol)	ΔS (kJ/mol)	TΔS (kJ/mol)	ΔG (kJ/mol)
298	3,12E+03	8,046	3,36E-03	-30,250	-0,035	-10,378	-19,872
308	1,97E+03	7,586	3,25E-03	-30,250	-0,035	-10,726	-19,524
328	1,01E+03	6,918	3,05E-03	-30,250	-0,035	-11,422	-18,827
DTAB – Zeolite							
Tem. (K°)	K_L	ln K_L	1/T	ΔH (kJ/mol)	ΔS (kJ/mol)	TΔS (kJ/mol)	ΔG (kJ/mol)
298	8,98E+02	6,800	3,36E-03	-27,745	-0,037	-10,939	-16,806
308	5,98E+02	6,394	3,25E-03	-27,745	-0,037	-11,307	-16,439
328	3,20E+02	5,768	3,05E-03	-27,745	-0,037	-12,041	-15,705
Activated Carbon							
Tem. (K°)	K_L	ln K_L	1/T	ΔH (kJ/mol)	ΔS (kJ/mol)	TΔS (kJ/mol)	ΔG (kJ/mol)
298	5,63E+03	8,636	3,36E-03	4,275	0,086	25,643	-21,368
308	5,79E+03	8,664	3,25E-03	4,275	0,086	26,503	-22,228
328	6,56E+03	8,789	3,05E-03	4,275	0,086	28,224	-23,949

The negative ΔG° values of 2,4-D adsorption on organo-zeolites and activated carbon is due to the fact that the sorption processes are spontaneous nature at all temperature. The negative value of ΔH° for organo-zeolite exhibit the exothermic character of adsorption, whereas the positive value of ΔH° for activated carbon exhibit the endothermic character of adsorption. Adsorption of 2,4-D on organo-zeolites show negative ΔS° values which means that decreasing the randomness at the solid–solution interface during adsorption

Higher negative values of ΔG° reflect more energetically favorable sorption. Therefore, adsorption of 2,4-D on activated carbon at 55° C was the most favorable sorption compared with adsorption on organo-zeolites.

The magnitude of the activation energy yields information on whether the adsorption is mainly physical or chemical. According to Alkan et al.(2004), enthalpy change due to chemisorption takes value between 40 and 120 kJ/mol. Therefore, the low value of ΔH° obtained from experiments indicates that adsorption of 2,4-D is likely due to physisorption.

Calculated activation energies for propanil adsorption on organo-zeolites and activated carbon are given in Table 8.31.

Table 8.31 Thermodynamic Parameters for Adsorption of Propanil

HTAB – Zeolite							
Tem. (K°)	K_L	ln K_L	1/T	ΔH (kJ/mol)	ΔS (kJ/mol)	TΔS (kJ/mol)	ΔG (kJ/mol)
298	1,54E+04	9,642	3,36E-03	29,256	0,179	53,236	-23,979
308	2,48E+04	10,119	3,25E-03	29,256	0,179	55,022	-25,766
328	4,61E+04	10,739	3,05E-03	29,256	0,179	58,595	-29,339
DTAB – Zeolite							
Tem. (K°)	K_L	ln K_L	1/T	ΔH (kJ/mol)	ΔS (kJ/mol)	TΔS (kJ/mol)	ΔG (kJ/mol)
298	4,38E+03	8,385	3,36E-03	21,152	0,142	42,282	-21,130
308	8,33E+03	9,028	3,25E-03	21,152	0,142	43,701	-22,549
328	1,02E+04	9,230	3,05E-03	21,152	0,142	46,539	-25,386
Activated Carbon							
Tem. (K°)	K_L	ln K_L	1/T	ΔH (kJ/mol)	ΔS (kJ/mol)	TΔS (kJ/mol)	ΔG (kJ/mol)
298	1,03E+04	9,240	3,36E-03	33,804	0,191	56,897	-23,094
308	1,97E+04	9,888	3,25E-03	33,804	0,191	58,807	-25,003
328	3,72E+04	10,524	3,05E-03	33,804	0,191	62,625	-28,821

From the Table 8.31, it can be seen that, the ΔG° values for organo-zeolites and activated carbon are negative which means that the sorption processes are spontaneous nature at all temperature.

Adsorption processes of propanil on organo-zeolites and activated carbon are endothermic at all temperatures. The positive values of ΔH° for organo-zeolites and activated carbon exhibit the endothermic process at all temperatures. Low value of enthalpy (ΔH°) obtained from experiments indicates that adsorption of propanil is likely due to physisorption.

Higher negative value of ΔG° was obtained with HTAB-Zeolite at 55° C. Therefore, adsorption of propanil on HTAB-Zeolite at 55° C was the most favorable sorption compared with adsorption experiments on DTAB-Zeolite and activated cabon.

Calculated activation energies for diazinon adsorption on organo-zeolites and activated carbon are given in Table 8.32.

Table 8.32 Thermodynamic Parameters for Adsorption of Diazinon

HTAB – Zeolite							
Tem. (K°)	K_L	ln K_L	1/T	ΔH (kJ/mol)	ΔS (kJ/mol)	TΔS (kJ/mol)	ΔG (kJ/mol)
298	4,07E+03	8,311	3,36E-03	-22,949	-0,006	-1,829	-21,120
308	5,19E+03	8,554	3,25E-03	-22,949	-0,006	-1,890	-21,059
328	1,92E+03	7,560	3,05E-03	-22,949	-0,006	-2,013	-20,936
DTAB – Zeolite							
Tem. (K°)	K_L	ln K_L	1/T	ΔH (kJ/mol)	ΔS (kJ/mol)	TΔS (kJ/mol)	ΔG (kJ/mol)
298	8,77E+03	9,079	3,36E-03	-24,602	-0,006	-1,688	-22,913
308	9,84E+03	9,194	3,25E-03	-24,602	-0,006	-1,745	-22,857
328	3,82E+03	8,248	3,05E-03	-24,602	-0,006	-1,858	-22,743
Activated Carbon							
Tem. (K°)	K_L	ln K_L	1/T	ΔH (kJ/mol)	ΔS (kJ/mol)	TΔS (kJ/mol)	ΔG (kJ/mol)
298	1,82E+04	9,809	3,36E-03	-29,783	-0,018	-5,391	-24,392
308	1,35E+04	9,510	3,25E-03	-29,783	-0,018	-5,572	-24,211
328	6,16E+03	8,726	3,05E-03	-29,783	-0,018	-5,934	-23,849

The negative values of ΔH° and ΔG° for organo-zeolites and activated carbon indicate that the sorption processes are exothermic and spontaneous nature at all temperature.

The negative value of ΔS° confirms the decreased randomness at the solid–solution interface during adsorption.

From the calculated ΔG° values, it was found that, adsorption of diazinon on activated carbon at 25° C was the most favorable sorption compared with adsorption experiments on organo-zeolites.

ΔH° values obtained from experiments are low which means that adsorption of diazinon is likely due to physisorption.

Calculated activation energies for fenitrothion adsorption on organo-zeolites and activated carbon are given in Table 8.33.

Table 8.33 Thermodynamic Parameters for Adsorption of Fenitrothion

HTAB – Zeolite							
Tem. (K°)	KL	ln KL	1/T	ΔH (kJ/mol)	ΔS (kJ/mol)	TΔS (kJ/mol)	ΔG (kJ/mol)
298	4,24E+04	10,655	3,36E-03	-27,335	-0,005	-1,443	-25,892
308	1,76E+04	9,776	3,25E-03	-27,335	-0,005	-1,491	-25,844
328	1,41E+04	9,554	3,05E-03	-27,335	-0,005	-1,588	-25,747
DTAB – Zeolite							
Tem. (K°)	K_L	ln K_L	1/T	ΔH (kJ/mol)	ΔS (kJ/mol)	TΔS (kJ/mol)	ΔG (kJ/mol)
298	1,474E+04	9,598	3,36E-03	-24,137	-0,002	-0,576	-23,561
308	8,575E+03	9,057	3,25E-03	-24,137	-0,002	-0,595	-23,542
328	5,811E+03	8,668	3,05E-03	-24,137	-0,002	-0,634	-23,503
Activated Carbon							
Tem. (K°)	K_L	ln K_L	1/T	ΔH (kJ/mol)	ΔS (kJ/mol)	TΔS (kJ/mol)	ΔG (kJ/mol)
298	3,06E+04	10,329	3,36E-03	-27,247	-0,008	-2,462	-24,785
308	9,35E+03	9,143	3,25E-03	-27,247	-0,008	-2,545	-24,703
328	9,67E+03	9,177	3,05E-03	-27,247	-0,008	-2,710	-24,537

As it is seen from Table 8.33, calculated ΔH° and ΔG°values for organo-zeolites and activated carbon are negative which indicate that the sorption processes are exothermic and spontaneous nature at all temperature.

The negative value of ΔS° confirms the decreased randomness at the solid–solution interface during adsorption.

HTAB-Zeolite at 25° C was found as the most favorable sorption compared with adsorption experiments on DTAB-Zeolite and activated carbon.

Low value of ΔH° obtained from experiments indicates that adsorption of fenitrothion is likely due to physisorption.

Calculated activation energies for trifluralin adsorption on organo-zeolites and activated carbon are given in Table 8.34.

Table 8.34 Thermodynamic Parameters for Adsorption of Trifluralin

HTAB – Zeolite							
Tem. (K°)	K_L	ln K_L	1/T	ΔH (kJ/mol)	ΔS (kJ/mol)	TΔS (kJ/mol)	ΔG (kJ/mol)
298	2,00E+05	12,206	3,36E-03	24,848	0,185	55,161	-30,313
308	2,98E+05	12,605	3,25E-03	24,848	0,185	57,012	-32,164
328	5,07E+05	13,136	3,05E-03	24,848	0,185	60,714	-35,866
DTAB – Zeolite							
Tem. (K°)	K_L	ln K_L	1/T	ΔH (kJ/mol)	ΔS (kJ/mol)	TΔS (kJ/mol)	ΔG (kJ/mol)
298	2,27E+04	10,030	3,36E-03	10,481	0,118	35,211	-24,731
308	2,30E+04	10,043	3,25E-03	10,481	0,118	36,393	-25,912
328	3,27E+04	10,395	3,05E-03	10,481	0,118	38,756	-28,275
Activated Carbon							
Tem. (K°)	K_L	ln K_L	1/T	ΔH (kJ/mol)	ΔS (kJ/mol)	TΔS (kJ/mol)	ΔG (kJ/mol)
298	7,99E+04	11,289	3,36E-03	21,230	0,166	49,356	-28,126
308	1,24E+05	11,728	3,25E-03	21,230	0,166	51,012	-29,782
328	1,80E+05	12,101	3,05E-03	21,230	0,166	54,324	-33,095

The negative value of $\Delta G°$ for organo-zeolites and activated carbon indicate that the sorption processes are spontaneous nature at all temperature.

The positive values of $\Delta H°$ for organo-zeolites and activated carbon exhibit the endothermic process at all temperatures.

The positive $\Delta S°$ confirms the increased randomness at the solid-liquid interface during adsorption.

Higher negative value of $\Delta G°$ gives the information about favorable sorption. Therefore, adsorption of trifluralin on HTAB-Zeolite at 55° C was found as the most favorable sorption compared with adsorption experiments on DTAB-Zeolite and activated carbon.

Adsorption characteristic of trifluralin is found to be physisorption on the basis of low value of $\Delta H°$ obtained from experiments.

CHAPTER 9

CONCLUSION

In the light of the experimental results, the following conclusions may be drawn:

1. Na-clinoptilolite, quartz and heulandite were the main minerals test of the zeolite sample studied. Its Si/Al ratio and theoretical cation exchange capacity (TCEC) were found as 4.52 and 2.76 meq/g respectively. External water of zeolite released up to 150 °C, and loosely bound water was lost rapidly up to 200 °C. Total weight loss of the sample was reached to 15.4% at 1000 °C. Average pore diameter was found as 0.041µm, density and surface area of zeolite were found to be 2.10 g/cm^3 and 40.79 m^2/g respectively. The surface charge of zeolite was found as negative at all pH values (1-12); its zeta potential increased to about -35mV with increasing the pH of the suspension.

2. 0.1 M HCl concentration was determined as the optimum concentration of acid for the activation of zeolite without breaking the structure. 300° C was obtained as the optimum temperature for thermal activation.

3. Cationic surfactant adsorption capacity of natural zeolite was found as $2x10^{-4}$ mol/g and $1x10^{-4}$ mol/g for hexadecyltrimethyl ammonium bromide (HTAB) and dodecyltrimethyl ammonium bromide (DTAB) respectively. Cationic surfactant adsorption capacity of acid activated zeolite was lower than that of natural zeolite whereas capacity of thermal activated zeolite was not different from the natural zeolite. In addition zero point of charge of sample was occurred at concentration of $5x10^{-5}$ mol/L for HTAB and $6x10^{-3}$ mol/L for DTAB.

4. Adsorption isotherm of cationic surfactants on natural zeolite were best described by Langmuir isotherm model considering the better correlation between theoretical and experimental data. It was found that the adsorption of cationic surfactant onto natural zeolite could be best fitted by the pseudo second-order model.

5. HTAB adsorption on natural zeolite is decreased while DTAB adsorption is increased with increasing temperature as in the range of 25° C - 55° C. The negative values of $\Delta H°$ and $\Delta G°$ for HTAB exhibit the exothermic and spontaneous nature of the sorption process at all temperatures respectively. The positive value of $\Delta H°$ and the negative value of $\Delta G°$ for DTAB exhibit the endothermic and spontaneous nature of the sorption process at all temperatures respectively.

6. It was found that pesticides adsorption capacity of organo-zeolite and activated carbon increased with increasing initial concentration of pesticide.

7. It was observed that 2,4-D adsorption capacity of organo-zeolite decreased with increasing temperature while adsorption capacity of activated carbon increased with increasing temperature. Propanil and trifluralin adsorption capacity of organo-zeolite and activated carbon increased with increasing temperature whereas diazinon and fenitrothion adsorption capacity of organo-zeolite and activated carbon decreased with increasing temperature.

8. Adsorption isotherm of 2,4-D on organo-zeolites and activated carbon were best described by Langmuir isotherm model. Propanil adsorption isotherm on DTAB-Zeolite was best described by Langmuir isotherm model. The adsorption data obtained from HTAB-Zeolite and activated carbon fit well to both Langmuir and Freundlich isotherm. Adsorption isotherms of diazinon, fenitrothion and trifluralin on organo-zeolites and activated carbon were best described by Freundlich isotherm model.

9. Adsorption of 2,4-D on HTAB-Zeolite and activated carbon could be best fitted by the pseudo second-order model. However, the correlation coefficient of the second order model for adsorption of 2,4-D on DTAB-Zeolite is low (R^2

< 0.73), and the calculated q_e values obtained from the first order kinetic model was not reasonable. Adsorption of propanil, diazinon, fenitrothion and trifluralin on organo-zeolites and activated carbon were best fitted by the pseudo second-order model.

10. It was found that, adsorption of 2,4-D on organo-zeolites was exothermic and spontaneous at all temperature. However, adsorption of the substance on activated carbon was found to be endothermic sorption at all temperatures. The positive values of $\Delta H°$ and the negative values of $\Delta G°$ for adsorption of propanil and trifluralin on organo-zeolites and activated carbon indicate that the sorption processes were endothermic and spontaneous at all temperature. The negative values of $\Delta H°$ and $\Delta G°$ for adsorption of diazinon and fenitrothion on organo-zeolites and activated carbon indicate that the sorption processes were exothermic and spontaneous at all temperature. The low value of $\Delta H°$ obtained from experiments indicates that adsorption of pesticides are likely due to physisorption.

11. Finally it can be said that favorable sorption processes were obtained for 2,4-D adsorption on activated carbon at 55°C, for propanil and trifluralin adsorption on HTAB-Zeolite at 55°C, for diazinon adsorption on activated carbon at 25°C, and for fenitrothion adsorption on HTAB-Zeolite at 25°C.

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2- Lüle, G.M. “*Aktive Edilmiş Zeolit Kullanılarak Atık Sulardan Fenol Bileşiklerinin Uzaklaştırılması*” 3. Madencilik ve Çevre Sempozyumu. pp. 185-190. **11-12 Haziran 2009**
3- Lüle, G.M. Özbayoğlu, G. *“Heavy Metal Removal from Waste Water by using Natural and Modified Zeolite*” 11. th International Mineral Processing Symposium. pp. 693-699. **21-23 Ekim 2008**
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FIELD OF INTEREST

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