INVESTIGATION OF HEAVY METAL ADSORPTION OF CHROMIUM AND ZINC IONS BY NATURAL ZEOLITES AS ADSORBENT

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บทคัดย่อ

ชื่อเรื่อง : การศึกษาการดูดซับโลหะหนักของโครเมียมและสังกะสีไอออนด้วยซีโอไลต์ธรรมชาติที่ใช้เป็นตัวดูดซับ
โดย : อาทิตย์ จิโรจน์ภากร
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ศัพท์สำคัญ : การดูดซับ โครเมียม สังกะสี ซีโอไลต์ธรรมชาติ ไอโซเทอร์มการดูดซับ

การศึกษานี้ได้ประยุกต์ใช้ซีโอไลต์ธรรมชาติของไทยซึ่งพบบริเวณจังหวัดสงขลาจำนวน 7 ชนิด โดยทราบชนิดของซีโอไลต์และกำหนดชื่อเป็น มอร์ดีไนต์ (A), คาโอลิไนต์ (B), คาโอลิไนต์ 1เอ็ม ดี (C), คาโอลิไนต์ (D), คลินอพติโลไลต์ (E), คลินอพติโลไลต์ (F) และ คลินอพติโลไลต์ (G), เพื่อใช้ในการศึกษาการดูดซับโครเมียม (III) และสังกะสี (II) จากสารละลายที่เตรียมในระดับห้องปฏิบัติการด้วยวิธี batch ผลการศึกษาพบว่าซีโอไลต์ธรรมชาติชนิด A, B, C และ D มีประสิทธิภาพการดูดซับโครเมียม (III) ได้เป็นอย่างดีที่ 95.60%, 92.73%, 88.90% และ 92.49% ตามลำดับ ส่วนประสิทธิภาพการดูดซับสังกะสี (II) พบว่ามีค่า 82.38%, 57.84%, 48.19% และ 60.75% ตามลำดับ สภาวะที่เหมาะสมสำหรับการดูดซับโครเมียม (III) และสังกะสี (II) คือแขวนลอยซีโอไลต์ธรรมชาติในสารละลาย 5.00 ppm โครเมียม (III) ที่ pH 7.0 ในปริมาณ 20.0 กรัมต่อลิตร สำหรับซีโอไลต์ A และ 30.0 กรัมต่อลิตร สำหรับซีโอไลต์ B, C และ D และแขวนลอยซีโอไลต์ธรรมชาติในสารละลาย 5.00 ppm สังกะสี (II) ที่ pH 7.0 ในปริมาณ 30.0 กรัมต่อลิตร สำหรับซีโอไลต์ A, B, C และ D ใช้เวลา 1 ชั่วโมงในการดูดซับ และทำการรบกวนระบบที่เวลา 30 นาที เป็นเวลา 30 วินาที จากการศึกษาไอโซเทอร์มของการดูดซับของโลหะทั้ง 2 ด้วย ซีโอไลต์ธรรมชาติ A, B, C และ D พบว่าการดูดซับมีความสอดคล้องตามแลงเมียร์ไอโซเทอร์มมากกว่าฟรอยด์ลิชไอโซเทอร์ม ซึ่งแสดงให้เห็นว่าสามารถประยุกต์ใช้ซีโอไลต์ธรรมชาติของไทยเพื่อดูดซับโครเมียม (III) และสังกะสี (II) ในการบำบัดน้ำเสียได้จริงด้วยต้นทุนที่ถูกและกระบวนการบำบัดที่เป็นมิตรต่อสิ่งแวดล้อม

ABSTRACT

TITLE : INVESTIGATION OF HEAVY METAL ADSORPTION OF CHROMIUM AND ZINC IONS BY NATURAL ZEOLITES AS ADSORBENT
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KEYWORDS : CHROMIUM (III) ION / ZINC (II) ION / NATURAL ZEOLITES / ADSORPTION / ADSORPTION ISOTHERM

7 Thai natural zeolites with classified name, mordenite (A), kaolinite (B), kaolinite 1Md (C), kaolinite (D), clinoptilolite (E), clinoptilolite (F) and clinoptilolite (G), found in Songkhla province have been applied to investigate the adsorption of Cr^{3+} and Zn^{2+} from aqueous solution on laboratory scale by batch adsorption experiment. The results show that natural zeolites A, B, C and D are successfully use to adsorb Cr^{3+} with the adsorption efficiency of 95.60%, 92.73%, 88.90% and 92.49%, respectively. The adsorption efficiencies of Zn^{2+} are 82.38%, 57.84%, 48.19% and 60.75% for natural zeolites A, B, C and D, respectively. The optimum condition for adsorption of Cr^{3+} is obtained by suspended each 20.0 g/l of zeolite A and 30.0 g/l of zeolites B, C and D in 5.00 ppm Cr^{3+}solution at pH 7.0. While, suspension of each 30.0 g/l of zeolites A, B, C and D in 5.00 ppm zinc solution at pH 7.0 are the optimum condition for adsorption of Zn^{2+}. An hour with systematic perturbation at the time of 30 minutes for 30 seconds was the optimum adsorption time for both metal ions. Based on the preliminary chromium and zinc adsorption studies, the obtained isotherm is consistent to the Langmuir isotherm. The investigated result indicated that the use of Thai natural zeolite is reasonable for suitably Cr^{3+} and Zn^{2+} adsorption in wastewater treatment with low cost and environmentally friendly chemical process.

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ABBRIVIATIONS

AAS = Atomic Absorption Spectrometer
b = Langmuir constants related to sorption energy
C_{ads} = the number of metal ions adsorbed onto zeolite
C_e = the equilibrium concentration of metal ions in solution
C_i = the initial metal ions concentration
Clin = Clinoptilolite
Cr^{3+} = chromium (III)
Cr^{6+} = chromium (VI)
DI = deionized
g/l = gram per liter
hrs = hours
K = a parameter related to the temperature
M = molar
min. = minute
n = a characteristic constant for the adsorption system under study
nm. = nanometer
no. = number
ppm = part per million
Q = Langmuir constants related to sorption capacity
R^2 = determination coefficient
sec. = second
SD = standard deviation
Zn^{2+} = zinc (II)

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Water pollution concerned with the heavy metals contamination is a major serious problem in Thailand. It is known that elevated concentrations of them are detrimental for aquatic living organism, through the food chain, toxic for all living organisms especially human who related with water (Kocaoba et al., 2007).

Chromium and zinc are classified as heavy metals and commonly associated with water pollution. The presence of these metals in water can be a result of leaching from soil and ground water or discharge from diverse commercial factories that can generate toxic wastes. There are a great variety of industrial processes that generate chromium contamination such as mining manufacture, metallurgical or electronic components, some catalyst and by-products of electroplating or pigments and paints. These toxic heavy metals have been discharged into the environment as industrial wastes, causing serious soil and water pollution. The effluent from these industries may contain chromium at concentrations ranging from ten to hundreds of ppm that would endanger public health and the environment if discharged without adequate treatment. According to Industrial Effluent Standards of the Ministry Natural Resources and Environment of Thailand, the upper limit of Cr^{3+} and Cr^{6+} in wastewaters are 0.75 and 0.25 ppm, respectively (http://www.pcd.go.th/info_serv/en_reg_std_water04.html).

There are 2 forms of chromium which are widely found in an aqueous and tend to accumulate in organisms, causing numerous diseases and disorders. Cr^{3+} plays an essential role plant and animal metabolism, while Cr^{6+} is highly toxic, mutagenic, and carcinogenic. In cell induce the formation of reactive oxygen species that damage cellular membrane. Therefore, the spontaneous oxidation process in nature is responsible for upsurge of research in alternative removal technologies for Cr^{3+} ions that are widely applied in industry (Barros et al., 2006).

For zinc species, there is only Zn^{2+} form when dissolving in aqueous solution. Although trace amount of zinc is essential for enzyme system in human body, large amount of Zn in human body will cause the disorder of liver. Zinc manufacturing and other industries release large quantities of zinc during production such as production of sun block lotion from zinc oxide, alloy manufacturing and the increasing demand for alkaline zinc manganese batteries, instead of mercury batteries, brings serious problems when those batteries are not disposed off properly. Another source of zinc contamination can be due to the flooding of zinc ore mines into the environment. The standard value of zinc industrial effluent in wastewaters is 5.00 ppm (http://www.pcd.go.th/info_serv/en_reg_std_water04.html).

Therefore, intense scientific research is being directed towards the implementation of novel approaches dealing with the efficient removal of toxic metals from wastewaters. Several treatment technologies, such as chemical precipitation, ultra filtration, adsorption, ion-exchange, reverse osmosis and electro dialysis have been developed for removal of heavy metals in general from solution phase (Carvalho et al., 2005). A number of adsorbent materials have been studied for their capacity to remove heavy metals, including activated carbon, activated alumina, ion-exchange resins, crushed coals, natural zeolites, synthesized zeolites, clay minerals and other aluminosilicates (Adrain et al., 1999). Some of these materials such as ion exchange resins are totally effective but expensive and others such as coal and straw are inexpensive but ineffective.

Among the various available cation exchangers, zeolites meet the requirements of good selectivity and acceptable capacity. Zeolites are micro porous crystalline hydrated aluminosilicates that can be considered as inorganic polymers built from an infinitely extending three-dimensional network of tetrahedral TO_4 units, where T is Si or Al, which form interconnected tunnels and cages and provide large internal and external surface areas for ion-exchange (http://www.en.wikipedia.org/Zeolites). Each aluminum ion presenting in the zeolite framework yields a net negative charge which is balanced by an extra framework cation, usually from the group IA or IIA such as Na^+, K^+, Ca^{2+} and Mg^{2+}. Water will move freely in and out of zeolite pores but the framework remains rigid. The porous zeolite is host to water molecules and ions of positive charge and the ability to exchange cation is one important property of them. As the balancing cations are not rigidly fixed at specific locations within the hydrated unit cell, it is possible to effective exchange with external cations in solution. Some parameters such as the hydration ratio of both co-ion and in-going ion as well as temperature and the three dimensional zeolite framework highly influence the ion exchange mechanism.

As others heavy metal cations, chromium and zinc are removed from aqueous media though ion exchange based processes using zeolites have been proposed as an alternative method Based on the properties of high sorption capacity and selectivity result from high porosity and sieving properties. Zeolites are capable to exchange cations is one of their most useful properties and determines their ability to remove heavy metals from industrial wastewater (Kocaoba et al., 2007).

Clinoptilolite, chabazite, heulandite, kaolinite and mordenite are the typically natural zeolite naturally occurring in many parts of the world near volcanic rock resource. In the south of Thailand, there are also the natural zeolite resources of the Southeast Asia. There has been found very effective in removing heavy metal dissolving in wastewater. Many researchers have investigated various aspects of heavy metal removal from synthetic aqueous solution and wastewater by using natural zeolites as adsorbent.

1.2 OBJECTIVES

As seen from the background, zeolites can be used for the removal of some heavy metals from wastewater. The natural zeolite samples from Songkhla province, in the south of Thailand, show good property to remove many metal cations in wastewater. In this study, the adsorption properties of the natural zeolite with respect to chromium and zinc in aqueous solution in laboratory scale were investigated with the objective of;

1.2.1 To perform the preliminary adsorption study of chromium and zinc adsorption efficiency by using 7 natural zeolites.

1.2.2 To study the effects of zeolites amount, adsorption time, initial solution pH and initial metal ion concentration on establish the optimum condition for the adsorption of chromium and zinc by natural zeolites.

1.2.3 To investigate the adsorption isotherms, Langmuir and Freundlich isotherms, for the adsorption of chromium and zinc from aqueous solution by natural zeolites.

CHAPTER 2

LITERATURE REVIEW

2.1 WATER POLLUTION

Water pollution is a large set of adverse effects on water sources for example ground water, oceans, and rivers caused by human activities. It is called polluted when it is unable to be used for what one wants it to be used for. It is a major problem in many countries which have water resources and have been suggested that it is the leading cause of deaths and diseases.

Water pollution has many causes and characteristics such as industries discharge a variety of pollutants in their wastewater including some heavy metals, resin materials, toxic organic compounds, oils and nutrients. All discharges can also have thermal effects as a major cause for water pollutant especially these too reduce the available oxygen. Silt-bearing runoff from many activities including construction sites, deforestation and agriculture can inhibit the penetration of sunlight through the water column, restricting photosynthesis and causing blanketing of the lake or river bed, in turn damaging ecological systems. And other major cause is an increasing in nutrient loading may lead to eutrophication (Eutrophication is the fertilization of surface water by nutrients that were previously scarce.). Some organic wastes such as sewage impose high oxygen demands on the receiving water leading to oxygen depletion with potentially severe impacts on the ecological system.

2.2 WATER TREATMENT AND WATER PURIFICATION

Water treatment describes as a process used to make water more acceptable for use such as drinking water, industrial processes, medical and many other uses. The aim of all water treatment process is to remove present components in the water, improving it quality before use. The goal of treatment process is to allow treated water to discharge into the natural environment without adverse ecological impact. These processes may be physical such as settling, chemical such as disinfection or coagulation, or biological such as lagooning, slow sand filtration or activated sludge.

Water purification is the next process followed by water treatment for removal of contaminants from untreated water to produce drinking water that is pure enough for its intended use, most commonly human consumption.

2.3 HEAVY METAL

There are so many reasons to define the meaning or definition of heavy metals for example the definition below;

A heavy metal is any of a number of higher atomic weight elements which has the properties of a metallic substance at room temperature. There are several different definitions concerning which elements fall in this class designation. Alternative terms are metal or semi-metal. According to this definition, heavy metals are a group of elements between copper and bismuth on the periodic table of the elements-having specific gravities greater than 4.0. A more strict definition increases specificity to metals heavier than the rare earth metals, which are at the bottom of the periodic table. None of these are essential elements in biological systems and additionally, most of the better known elements are toxic in low concentrations. Thorium and uranium are occasionally included in this classification as well, but they are more often referred to as “radioactive metals”. Also, often the elements beyond mercury, the actinides such as uranium and plutonium, are not excluded from the heavy metals (Butler and Harrod., 1989).

Any toxic metals may be called “heavy metals”, irrespective of their atomic mass or density. As seen in these definitions, “heavy metals” is an ambiguous term, not necessarily associated with any specific set of elements, and therefore not necessarily implying any common set of properties such as high toxicity and high atomic weight.

However living organisms require trace amounts of some heavy metals, including iron, cobalt, copper, manganese, molybdenum, vanadium, strontium, and zinc for use as biological function in their system, but excessive levels can be detrimental to the organism. Other heavy metals such as mercury, lead and cadmium are toxic metals because they have no pathway to use and get rid of or beneficial effect on organisms, and their accumulation over time in the mammalian bodies can cause serious diseases.

2.4 CHROMIUM

Chromium is a chemical element which has the symbol Cr and atomic number 24. It is a steel-gray, lustrous, hard metal that takes a high polish and has a high melting point. It is also odorless, tasteless, and malleable (http://www.en.wikipedia.com/chromium).

Chromium is a naturally occurring element found in rocks and soil. It is present in the environment in several different forms; the most common is trivalent chromium [Cr (III) or Cr^{3+}] and hexavalent chromium [Cr (VI) or Cr^{6+}]. Chromium is steel-grey, lustrous and hard. It is used on a large scale in the metallurgical and chemical industries. Metallurgical industry commonly uses chromium for the production of stainless steels, alloy cast iron and nonferrous alloys as well as for plating steel. In the chemical industry, Cr^{3+} and Cr^{6+} are used primarily in pigments, metal finishing and electroplating as well as wood preservatives and leather tanning. In the past, chromium was also used in cooling towers as a rust and corrosion inhibitor and as a fungicide.

2.4.1 Applications of chromium

2.4.1.1 In metallurgy, it is used as corrosion resistance and a shiny finish:

1) It is used as an alloy constituent such as in stainless steel.
2) It is used in chrome plating.

2.4.1.2 Chromium is used as dyes and paints:

1) Cr_2O_3 is a metal polish known as green rouge.
2) Chromium salts make an emerald green color of glass.
3) Chromium is used in producing synthetic rubies.
4) Chromium also makes a brilliant yellow for painting

2.4.1.3 Chromium is used as a catalyst.

2.4.1.4 Chromite is used to make molds for the firing of bricks.

2.4.1.5 Chromium salts are used in the tanning of leather.

2.4.1.6 Potassium dichromate is a chemical reagent, used in cleaning laboratory glassware and as a titrating agent. It is also used as a fixing agent for dyes in fabric.

2.4.1.7 Chromium (IV) oxide (CrO_2) is used to manufacture magnetic tape, where its higher coercively than iron oxide tapes gives better performance.

2.4.1.8 In medicine, using as a dietary supplement or slimming aided, usually as chromium (III) chloride, chromium (III) picolinate, chromium (III) polynicotinate or as an amino acid chelate, such as chromium (III) D-phenylalanine.

2.4.1.9 Chromium hexacarbonyl ($Cr(CO)_6$) is used as a gasoline additive.

2.4.2 Biological role of chromium

Cr^{3+} is required in trace amounts for sugar metabolism in humans (Glucose Tolerance Factor) and its deficiency may cause a disease called chromium deficiency.

In contrast, Cr^{6+} compounds can be toxic if orally ingested or inhaled. The lethal dose of poisonous Cr^{6+} compounds is about one half teaspoon of material. Most Cr^{6+} compounds are irritating to eyes, skin and mucous membranes. Chronic exposure to Cr^{6+} compounds can cause permanent eye injury, unless properly treated. Cr^{6+} is an established human carcinogen.

World Health Organization recommended maximum allowable concentration in drinking water for Cr^{6+} is 0.05 ppm. Cr^{6+} is also one of the substances whose use is restricted by the European Restriction of Hazardous Substances Directive.

As chromium compounds were used in dyes and paints and the tanning of leather, these compounds are often found in soil and groundwater at abandoned industrial sites, now needing environmental cleanup and remediation per the treatment of Brownfield land. Primer paint containing hexavalent chromium is still widely used for aerospace and automobile refinishing applications (Basaldella et al., 2007).

2.5 ZINC

Zinc is a metallic chemical element with the symbol Zn with atomic number 30 and moderately reactive, blue gray metal that tarnishes in moist air and burns in air with a bright bluish-green flame, giving off fumes of zinc oxide. It reacts with acids, alkalis and other non-metals. If not completely pure, zinc reacts with dilute acids to release hydrogen. The only one common oxidation state of zinc is +2.

Zinc is the 23rd most abundant element in the Earth's crust. The most heavily mined ores (sphalerite) tend to contain roughly 10% iron as well as 40-50% zinc. Minerals from which zinc is extracted include sphalerite (zinc sulfide), smithsonite (zinc carbonate), hemimorphite (zinc silicate), and franklinite (a zinc spinel). There are zinc mines throughout the world, with the largest producers being China, Australia and Peru (http://www.en.wikipedia.com/zinc).

2.5.1 Application of zinc

2.5.1.1 Producing of an alloy. The most widely used alloy of zinc is brass, in which copper is alloyed with anywhere from 9% to 45% zinc, depending upon the type of brass, along with much smaller amounts of lead and tin. Alloys of 85-88% Zn, 4-10% Cu and 2-8% Al find limited use in certain types of machine bearings. Alloys of primarily zinc with small amounts of copper, aluminum, and magnesium are useful in die casting as well as spin casting. An example of this is zinc aluminum. Similar alloys with the addition of a small amount of lead can be cold-rolled into sheets. An alloy of 96% Zn and 4% Al is used to make stamping dies for low production run applications where ferrous metal dies would be too expensive.

2.5.1.2 Zinc oxide is used as a white pigment in water colors or paints and as an activator in the rubber industry. As an over-the-counter ointment, it is applied as a thin coating on the exposed skin of the face or nose to prevent dehydration of the area of skin. It can protect against sunburn in the summer and windburn in the winter. Applied thinly to a baby's diaper area (perineum) with each diaper change, it can protect against rash. As determined in the Age-Related Eye Disease Study, it is part of an effective treatment for age-related macular degeneration in some cases.

2.5.1.3 Zinc is used as part of the containers of batteries. The most widespread such use is as the anode in alkaline batteries.

2.5.1.4 It is used as the anode or fuel of the zinc-air battery or fuel cell providing the basis of the theorized zinc economy.

2.5.1.5 Zinc is used as a sacrificial anode on boats and ships that use cathodic protection to prevent corrosion of metals that are exposed to sea water.

2.5.2 Biological role of zinc

Zinc is an essential element, necessary for sustaining all life. It is estimated that 3,000 of the hundreds of thousands of proteins in the human body contain zinc prosthetic groups, one type of which is the so-called zinc finger. In addition, there are over a dozen types of cells in the human body that secrete zinc ions and the roles of these secreted zinc signals in medicine and health are now being actively studied. Zinc ions are now considered neurotransmitters. Many cells in the salivary gland, prostate, immune system and intestine are other types using zinc signaling.

Zinc deficiency results from inadequate intake of zinc or inadequate absorption of zinc into the body. Signs of zinc deficiency include hair loss, skin lesions, diarrhea and wasting of body tissues. Eyesight, taste, smell and memory are also connected with zinc. A deficiency in zinc can cause malfunctions of these organs and functions. Congenital abnormalities causing zinc deficiency may lead to a disease called Acrodermatitis enteropathica. Conservative estimates suggest that 25% of the world's population is at risk of zinc deficiency.

Zinc supplementation has been shown to reduce diarrhea prevalence and mortality in children <5 years of age. Obtaining a sufficient zinc intake during pregnancy and in young children is a very real problem, especially among those who cannot afford a good and varied diet. Brain development is stunted by zinc insufficiency in utero and in youth.

It is rarely recognised that lack of zinc can contribute to acne. Leukonychia, white spots on the fingernails, are often seen as an indication of zinc deficiency. High dose of zinc, 30 mg for 1-3 times per a day, prevents dysmenorrhea.

2.5.3 Zinc toxicity

Even though zinc is an essential requirement for a healthy body, too much zinc can be harmful. Excessive absorption of zinc can also suppress copper and iron absorption. The free zinc ion in solution is highly toxic to plants, invertebrates and even vertebrate fish. Micro molar amounts of the free ion kill some organisms.

2.6 ZEOLITE

Zeolites (Greek, zein, "to boil" and lithos, "a stone") are hydrated aluminosilicate minerals and have a micro-porous structure.

The term was originally coined in the 18th century by a Swedish mineralogist named Axel Fredrik Cronstedt who observed upon rapidly heating a natural mineral that the stones began to dance about as the water evaporated. Using the Greek words which mean "stone that boils" he called this material zeolite. More than 150 zeolite types have been synthesized and 48 naturally occurring zeolites are known. Zeolites have an "open" structure that can accommodate a wide variety of cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+} and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. Some of the more common mineral zeolites are: analcime, chabazite, heulandite, natrolite, phillipsite and stilbite.

Natural zeolites form where volcanic rocks and ash layers react with alkaline groundwater. Zeolites also crystallized in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins. Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz or other zeolites. For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential.

Zeolites are the aluminosilicate members of the family of micro porous solids known as “molecular sieves”. The term molecular sieve refers to a particular property of these materials such as the ability to selectively sort molecules based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the diameters of the tunnels. These are conventionally defined by the ring size of the aperture, where the term “8 ring” refers to a closed loop that is built from 8 tetrahedral coordinated silicon (or aluminium) atoms and 8 oxygen atoms. These rings are not always perfectly flat and symmetrical due to a variety of effects, including strain induced by the bonding between units that are needed to produce the overall structure, or coordination of some of the oxygen atoms of the rings to cations within the structure. Therefore, the pore openings for all rings of one size are not identical (Bailey et al., 1999).

Zeolites are widely used as ion-exchange beds in domestic and commercial water purification, softening, and other applications. In chemistry, zeolites are used to separate molecules (only molecules of certain sizes and shapes can pass through), as traps for molecules so they can be analyzed.

Zeolites have the potential of providing precise and specific separation of gases including the removal of H_2O, NH_3, CO_2 and SO_2 from low-grade natural gas streams. Other separations including noble gases, N_2, O_2, freon and formaldehyde. However at present, the true potential to improve the handling of such gases in this manner remains unknown (Yang, Navrotsky and Wilkin., 2005).

2.7 APPLICATIONS OF ZEOLITE

There are several applications of zeolites in various activities such as

2.7.1 Petrochemical industry

Synthetic zeolites are widely used as catalysts in the petrochemical industry, for instance in fluid catalytic cracking and hydro-cracking. Zeolites confine molecules in small spaces, which cause changes in their structure and reactivity. The hydrogen form of zeolites (prepared by ion-exchange) is powerful solid-state acids and can facilitate a host of acid-catalyzed reactions, such as isomerisation, alkylation, and cracking. Catalytic cracking uses a furnace and reactor. First crude oil distillation fractions are heated in the furnace and passed to the reactor. In the reactor the crude meets with a catalyst such as zeolite. It goes through this step three times, each time getting cooler. Finally it reaches a step known as separator. The separator collects recycled hydrogen. Then it goes through fractionators and becomes the final item.

2.7.2 Agriculture

In agriculture, clinoptilolite (a naturally occurring zeolite) is used as a soil treatment. It provides a source of slowly released potassium. If previously loaded with ammonium, the zeolite can serve a similar function in the slow release of nitrogen. Cuban studies in the emerging field of "zeoponics" suggest that some crops may be grown in 100% zeolite or zeolite mixtures in which the zeolite is previously loaded or coated with fertilizer and micronutrients. Zeolites can also act as water moderators, in which they will absorb up to 55% of their weight in water and slowly release it under plant demand. This property can prevent root rot and moderate drought cycles. A potting soil with 12% clinoptilolite was shown to harvest morning dew and return it to the plant roots for reuse.

2.7.3 Detergents

The largest outlet for synthetic zeolite is the global laundry detergent market. This amounted to 1.44 million metric tons per year of anhydrous zeolite A in 1992.

2.7.4 Construction

Synthetic zeolite is also being used as an additive in the production process of warm mix asphalt concrete. The development of this application started in Europe (Germany) in the 1990s. It helps by decreasing the temperature level during manufacture and laying of asphalt concrete, resulting in lower consumption of fossil fuels, thus releasing less carbon dioxide, aerosols and vapors. Other than that the usage of synthetic zeolite in hot mixed asphalt leads to easier compaction and to a certain degree allows cold weather paving and longer hauls. When added to Portland cement as a Pozzolan, it can reduce chloride permeability and improve workability. It reduces weight and helps moderate water content while allowing for slower drying which improves break strength.

2.7.5 Aquarium keeping

Zeolites are marketed by pet stores for use as a filter additive in aquariums. In aquariums, zeolites can be used to absorb ammonia and other nitrogenous compounds. However, due to the high affinity of some zeolites for calcium, they may be less effective in hard water and may deplete calcium. Zeolite filtration is used in some marine aquaria to keep nutrient concentrations low for the benefit of corals adapted to nutrient-depleted waters.

2.7.6 Water softening (ion exchanger)

Zeolite can be used as ion exchanger in the process of drinking water purification. The process depends on the ability of granular materials, called zeolites, to exchange ions present in their structure for ions present in the water. As the hard water percolates through the zeolite bed, the calcium and magnesium ions in the water are exchanged for sodium ions in the bed, making the water soft. The calcium and magnesium ions are left attached to the zeolite grains. When the exchange capacity of the zeolite is exhausted, it can be regenerated by passing a strong salt (sodium chloride) solution through it. The excess sodium in this solution causes the zeolite to give up the calcium and magnesium ions and take up a new supply of sodium ions. The wash water is then flushed out and the unit is ready to resume the softening process.

2.8 ADSORPTION

A process of adsorbate such as gas or liquid solute accumulates or bonds the chemical bonding on the surface of a solid or a liquid which is called as adsorbent, forming a molecular or atomic film of the adsorbate. It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term of adsorption encompasses both processes, while desorption is the reverse process.

Adsorption is indicative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Adsorption, ion exchange and chromatography are sorption processes in which certain adsorptives are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column.

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency because they are not wholly surrounded by other atoms. Thus it is energetically favorable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption (http://www.wikipedia.com/adsorption).

2.9 ADSORPTION ISOTHERM

Adsorption is usually described through isotherms, that are functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid).

Two important physiochemical aspects for the evaluation of the adsorption process as a unit operation are the equilibria of the adsorption and the kinetics. Equilibrium studies give the capacity of the adsorbent. The equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium. There are two types of adsorption isotherms which are popular and simply to perform: Langmuir adsorption isotherm and Freundlich adsorption isotherm.

2.10 FREUNDLICH ISOTHERM

Herbert Max Finley Freundlich, a German physical chemist, presented an empirical adsorption isotherm for non-ideal systems in 1906. The Freundlich Adsorption Isotherm is an adsorption isotherm which is a curve relating the concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact.

The Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as:

$$\log C_{ads} = 1/n \log C_e + \log K$$

Where;			
	C_e	is	the equilibrium concentration of adsorbate in solution
	C_{ads}	is	the concentration of adsorbate adsorbed onto zeolite
	K	is	a parameter related to the temperature
	n	is	a characteristic constant for the adsorption system under study

A plot of log C_{ads} as y-axis against log C_e as x-axis yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constants can be determined from the slope and the intercept.

K and 1/n are constants for a given adsorbate and adsorbent at a particular temperature. A value of n between 2 to 10 shows good adsorption. The numerical value of $1/n < 1$ indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations. This isotherm does not predict any saturation of the adsorbent by the adsorbates; thus infinite surface coverage is predicted mathematically, indicating multilayer adsorption on the surface (Trgo, Peric and Medvivovic., 2004).

2.11 LANGMUIR ISOTHERM

Whenever an adsorbate such as gas or some particles in solution contacts with a surface of solid phase called as adsorbent, there will be an equilibrium established between the molecules in the gas phase and the corresponding adsorbed species (molecules or atoms) which are bound to the surface of the solid.

As with all chemical equilibrium, the position of equilibrium will depend upon a number of factors:

(1) The relative stabilities of the adsorbed and gas phase species involved.
(2) The temperature of the system.
(3) The pressure of the gas above the surface.

In general, factors (2) and (3) exert opposite effects on the concentration of adsorbed species that is to say that the surface coverage may be increased by raising the gas pressure but will be reduced if the surface temperature is raised.

The Langmuir isotherm was developed by Irving Langmuir in 1916 to describe the dependence of the surface coverage of an adsorbed gas on the pressure of the gas above the surface at a fixed temperature. There are many other types of isotherm such as Temkin, Freundlich or Brunauer Emmett Teller (BET) which differ in one or more of the assumptions made in deriving the expression for the surface coverage; in particular, on how they treat the surface coverage dependence of the enthalpy of adsorption. Whilst the Langmuir isotherm is one of the simplest, it still provides a useful insight into the pressure dependence of the extent of surface adsorption (Wittayakun and Krisadanurak., 2004).

The Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption and is often expressed as:

$$C_e/C_{ads} = C_e/Q + 1/Qb$$

Where; C_e is the equilibrium concentration of adsorbate in solution

C_{ads} is the concentration of adsorbate adsorbed onto zeolite

Q is Langmuir constants related to sorption capacity

b is Langmuir constants related to sorption energy

The linear form can be used for linearization of experimental data by plotting C_e/C_{ads} as y-axis against C_e as-x axis over the entire concentration range of investigated adsorbate. The Langmuir constants Q and b can be evaluated from the slope and intercept of linear equation.

Maximum sorption capacity (Q) represents monolayer coverage of adsorbate with adsorbent and b represents enthalpy of sorption and should vary with temperature. Minimum value of b represents chemical bonding between adsorbate and adsorbent are strong and stable.

2.12 RESEARCH WORKS CONCERNING WITH HEAVY METAL ADSORPTION

Lee et al (2000) performed the conversion of coal fly ash obtained from glassy combustion residues in a power generation plant into synthetic zeolite. The effect of using different temperatures and NaOH concentration, five different zeolites were obtained: Na-P1, faujasite, hydroxy sodalite, analcime, and cancrinite. It is also showed greater potential for remove some heavy metal ions than the original fly ash and natural zeolites. Na-P1 exhibited the highest adsorption capacity with a maximum value of about 1.29 mmole Pb/g and had a strong affinity for Pb^{2+} ion. The metal ion selectivity of Na-P1 was determined as: $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$ consistent with the decreasing order of the radius of hydrated metal ion. The adsorption isotherm for Pb^{2+} by Na-P1 fitted the Freundlich rather than the Langmuir isotherm.

Bosso and Enzweiler (2002) applied scolecite to heavy metal removal (Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} and Cd^{2+}) from aqueous solution. It was found that the maximum retention values of metal ions increase substantially when the ratio of scolecite and solution is increased. The affinity of Cu^{2+} and Pb^{2+} for scolecite is discussed based on their free ionic forms such as their hydrated bivalent ions and their hydrolysis products. The remaining ions are retained as free ions.

Li, Alessi and Allen (2002) studied the influence of quaternary ammonium surfactants on sorption of Cs^{+}, Sr^{2+}, La^{3+}, Pb^{2+}, and Zn^{2+} on clinoptilolite. The sorption capacity and affinity for the zeolite decreased, indicating that presorbed cationic surfactants blocked sorption sites for metal ions, as the surfactant loading on the zeolite increased. Cs^{+} and Pb^{2+} sorption was affected to a small extent, indicating that selective sorption for Cs^{+} and specific sorption for Pb^{2+} play an important role in addition to cation exchange. Sorption of cationic surfactants on zeolite preloaded with different metal cations showed a strong correlation with the chain length of the surfactant tail group, while the roles of the charges and types of the metal cations were minimal.

Almaraz et al (2003) investigated the comparison of adsorption of aqueous Zn^{2+} in the concentration range of 0.0002-0.05 M at neutral pH on 2 synthetic zeolites between zeolite X and clinoptilolite. It is found that Na^{+} or K^{+} is probably exchanged with Zn^{2+} during adsorption process. The compared behavior of the 2 zeolites is discussed in terms of kinetic effects based on ionic radius values. A co-adsorption test carried on with a 50-60% Zn^{2+} 0.001 M Pb^{2+}0.001 M solution shows that lead does not occupy the same sites as zinc because the content of zinc fixed on the zeolite sample exactly corresponds to the result obtained with a pure 0.001 M Zn^{2+}solution. All these data clearly showed that zeolite surface reactivity is greatly influenced by the mineral cage-like structure and particularly the presence of pockets, spaces and channels.

Haile, Olguin and Rios (2003) studied the removal of mercury from water by zeolites. The mercury sorption from aqueous solutions in the presence of Cu^{2+}, Ni^{2+} and Zn^{2+} onto unmodified Mexican zeolites and modified with cysteamine hydrochloride and cystamine dihydrochloride was investigated in acidic pH. Zeolites were characterized by TGA, SEM, XRD and FTIR techniques. The sorption kinetics behavior and the retention isotherms for mercury were determined in the natural and treated zeolites. It also found that amounts of sulfur on the modified zeolites were 0.375 (cysteamine hydrochloride) and 0.475 (cystamine dihydrochloride) mmol/g, which were not saturated to their total capacities of adsorption for the maximum concentration used (0.310 mM). Under the experimental conditions, the retention of mercury was the highest for the zeolitic minerals treated with the organic compounds, with adsorption capacities ranging from 0.0107 to 0.0509 mmol Hg/g.

Kocaoba et al (2003) investigated the Cr^{3+}, Co^{3+} and Cd^{2+} removal from wastewaters by natural and modified zeolites by using batch method. A Turkey natural clinoptilolite was pretreated with HCl and HNO_3 to improve the adsorption capacity for heavy metals. The removal efficiencies and kinetics of heavy metals such as Cr^{3+}, Co^{3+} and Cd^{2+} on natural and modified zeolites were determined. The kinetics of adsorption indicates the process to be diffusion controlled.

Ponizovskya, and Tsadilas (2003) studied the Pb^{2+} sorption by Alfisol and zeolite was studied at pH 3.0-5.0 to find the relationship between the amounts of Pb^{2+} retained and ions displaced from the soil into the solution. In Alfisol, Pb^{2+} sorption was accompanied by the increase in contents of Ca^{2+} and H^+ constituting about 2/3 and 1/3 of the total amount of displaced cations, respectively. Increase in pH enhanced sorption of Pb^{2+}. Hystersis of Pb^{2+} adsorption was observed in Alfisol. Clinoptilolite zeolite sorbed 20-30 times more Pb^{2+} than the soil. Pb^{2+} sorption by zeolite was not influenced by pH and was accompanied by the increase of Ca^{2+}, Na^+, and K^+ contents in solution, whereas amounts of displaced H^+ were negligible. The research indicates that Pb^{2+} retention both by Alfisol and zeolite can be viewed as the result of ion exchange reaction with strong (soil) or very strong (zeolite) specific binding of Pb^{2+}.

Sheta et al (2003) characterized the ability of 5 natural zeolites and bentonite minerals to adsorb and release Zn^{2+} and Fe^{2+}. It was found that Zn^{2+} sorption data followed the Langmuir equation. The ability for Zn^{2+} sorption was in the following order: chabazite > analcime > clinoptilolite1 > bentonite > clinoptilolite-2 > phillipsite. Fe^{2+} sorption data followed the S-type isotherm and the results were described by a Freundlich adsorption model. The results suggest that natural zeolites, particularly chabazite and bentonite minerals, have a high potential for Zn^{2+} and Fe^{2+} sorption with a high capacity for slow release fertilizers.

Trgo, Peric and Medvivovic (2003) studied the possibility of removing Zn^{2+} from wastewater by ion-exchange using natural zeolites as exchangers. Binding of Zn^{2+} into zeolite structure has been established by several reaction mechanisms as a fast chemical reaction of ion-exchange, accompanied by slower adsorption of different ionic species and possible precipitation or co-precipitation with the zeolite structure. The physicochemical phenomena such as hydrolysis and dissolution of surface layers are the result of interaction of zeolite with hydrogen or hydroxyl ions from the solution. It was found that complexation of OH^- with Zn^{2+} to form the zinc-hydroxide species strongly depends on pH value and affects the uptake mechanism as to lower dissolution of surface aluminosilicate layers.

Barros et al (2004) analyzed the ion exchange isotherm of K^+, Ca^{2+} and also Cr^{3+} with NaA zeolites at three temperatures: 30, 45 and 60°C. The NaA isotherms were favorable for the metal ions studied. Differences in shape are due to the different influence of temperature in the interaction of the in-going cation with the zeolite framework. As a consequence, sites of different energies were used in the exchange process, which provided non linear Kielland plots. Equilibrium constant (K), standard free energy (G^0), enthalpy (H^0) and enthopy (S^0) changes were measured and tabulated. K is directly proportional to the in-going ion charge. Concerning H^0, endothermic and exothermic exchanges were observed due to differences in the cation-framework interaction. The selectivity order based on the G^0 over the entire temperature range was $K^+ < Cr^{3+} < Ca^{2+}$, a consequence of different ion exchange mechanisms. It was also noted that the S^0 change increases with the polarizibility of the cations.

Erdem et al (2004) investigated the adsorption behavior of natural clinoptilolite with respect to Co^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+} using concentrations ranging from 100 to 400 ppm by batch method. The percentage adsorption and distribution coefficients (K_d) were determined for the adsorption system as a function of adsorbate concentration. The adsorption ratios of clinoptilolite metal cations match to Langmuir, Freundlich, and Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm data. It was found that the adsorption phenomena depend on charge density and hydrated ion diameter. According to the equilibrium studies, the selectivity sequence can be given as $Co^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$. These results show that natural zeolites hold great potential to remove cationic heavy metal species from industrial wastewater.

Peric, Trgo and Medvidovi (2004) study of a comparison of adsorption isotherm from the removal of Zn^{2+}, $Cu^{2+}$and Pb^{2+} from aqueous solutions by ion exchange on Croatian natural clinoptilolite. It was found that the efficiency of removal is higher for Pb^{2+} and Cu^{2+} than for Zn^{2+}. The adsorption isotherm equations; Langmuir-Freundlich, Redlich-Petersen, Toth, Dubinin-Radushkevich, modified Dubinin-Radushkevich, and Lineweawer-Burk were derived from the basic empirical equations, and used for calculation of ion exchange parameters. The best fitting of experimental results to the proposed isotherms was observed in models that assume that ionic species bind first at energetically most favorable sites, with multi-layer adsorption taking place subsequently.

Pitcher, Slade and Ward (2004) investigated the removal of heavy metals present in motorway storm water by batch methods on two zeolites (synthetic MAP and natural mordenite). It was found that synthetic zeolite MAP showed almost complete removal (>91%) of the Zn^{2+}, Cu^{2+}, Pb^{2+} and Cd^{2+} from both solutions. Mordenite was less effective at reducing the levels of heavy metals and exhibited a preference for $Pb^{2+} > Cu^{2+} > Zn^{2+} \sim Cd^{2+}$.

Buasri et al (2005) investigated Cu^{2+} and Zn^{2+} adsorption by using zeolite in order to obtain optimum condition for using of zeolite as adsorbent. The results of parameters that had influence in both ions adsorption were as follows. Increasing quantities of zeolite and time spending in ions adsorption, there would be more efficiency in the heavy metal ions adsorption. The pH values that were suitable for Cu^{2+} and Zn^{2+} adsorption are 5.0 and 7.0, respectively. If increasing more pH values, there was the complex compound sedimentation. The temperatures that were suitable for both heavy metal ions adsorption were 60 °C. Bringing the zeolite used in heavy metal ions adsorption back to use again in the suitable circumstance. It found that regenerated zeolite with NaCl solution, the efficiency in heavy metal ions adsorption were increasable in the suitable circumstance.

Bosco, Jimenez and Carvalho (2005) investigated the adsorption of Cr^{3+}, Ni^{2+}, Cd^{2+} and Mn^{2+} in synthetic aqueous effluents by natural Brazilian scoecite. Adsorption isotherms of single-metal solutions at 298, 313, and 333 K and effect of pH on the process were studied. Removal of metals from specific metal solutions is best described by a Freundlich isotherm, in which the values obtained for the K_f constants were in the following order: $Cr^{3+} > Mn^{2+} > Cd^{2+} > Ni^{2+}$. A Lagergren pseudo-second-order was the model that best described the sorption mechanism. The retention of metals was shown to be a function of the pH; the maximum binding capacity occurring at pH values around 6.0. Thermodynamic data indicate the spontaneity of the endothermic cation-exchange process.

Cozmuta et al (2005) developed some physico-chemical aspects presented along of Cu^{2+} adsorption in treatment of wastewaters using natural zeolites. In the experiments natural zeolites from Stoiana Paglia (Romania) has been used. Different concentrations of NaCl and HCl solutions were used for activation of zeolites. The increase of activation solutions concentrations indicates an intensification of specific adsorption of Cu^{2+} as consequence of energetic changes of the active centers spread on the tuff surface.

Faghihian et al (2005) investigated the adsorption of chromate ion (CrO_4^{2-}) form various chromate salt by using clinoptilolite compared with modified clinoptilolites. It is found that no affinity between unmodified zeolite surfaces and chromate anions, due to the fact those zeolite surfaces are negatively charged. Thus, adsorption of anions by unmodified clinoptilolites has not been given much attention. Then, after modification of clinoptilolite by different cations, the chromate anion was found to adsorb a considerable amount of the divalent anion chromate. Chromate adsorption was proportional to the K_{sp} of the chromate precipitate and the amount of the exchangeable cation. The amount of CrO_4^{2-} adsorbed was maximized when the Pb-exchanged form was used. Chromate desorption in deionized water indicated that between 2.50% and 18.60% of the adsorbed chromate was released depending upon the exchangeable cation. Some of the exchanged forms are candidate materials for adsorption and immobilization of chromate.

Prajaubsuk et al (2005) characterized the natural zeolite as an effective adsorbent derived from Songkhla province by XRD and XRF techniques. The results reveal that the XRD pattern of the zeolite corresponds to the clinoptiolite [$(Na, K, Ca)_5Al_6Si_{30}O_{72}.18H_2O$]. The XRF analysis shows the elemental compositions of the zeolite confirming the structural data obtained the XRD result. Adsorption of ammonia (NH_3) contaminated in wastewater on the zeolite has been carried out. Wastewater from 2 frozen seafood factories in Songkhla province was sampled. The method of phenolhypochlorite was applied to measure NH_3 contaminated in the wastewater. The results show that the optimum adsorption time is 24 hours and the ratio of zeolite per water sample is 20 g/l. NH_3 was removed from wastewater samples with an average removal efficiency of 65.6%. Consequently, the natural zeolite is successfully applicable for removal of NH_3 of wastewater from frozen seafood factories.

Wingenfelder et al (2005) studied on enhance the adsorption ability of clinoptilolite by modification of clinoptilolite with amine compound prepared in aqueous solution. Application of amine modified zeolite in removal Cd^{2+} and Pb^{2+} were obtained. It was found that adsorption of Cd^{2+} and Pb^{2+} on the zeolite was decreased with increasing amounts of amines sorbed. This reduction can be attributed to blockage of zeolite channels by amine molecules.

Akgul et al (2006) investigated the ability of natural clinoptilolite to remove Ag^+ from aqueous solution by batch adsorption experiments. The effects of pH, adsorption time, metal ion concentration and the acidic treatment on the adsorption process were examined. The optimum pH for adsorption was found to be 4.0. It was found that acid treatment has a substantial effect on the metal uptake. In adsorption studies, residual Ag^+ concentration reached equilibrium in a short duration of 45 mins. Maximum adsorption capacity, 33.23 mg Ag^+/g of zeolite, showed that the used adsorbent was suitable for silver removal from aqueous media. Adsorption phenomena appeared to follow Langmuir and Freundlich isotherms.

Barros et al (2006) investigated the removal of Cr^{3+}, Ca^{2+}, Mg^{2+} and K^+ in equilibrium isotherms and in tricomponent solutions (Cr/Ca/K, Cr/Ca/Mg and Cr/Mg/K). The experiment were performed in NaX and NaY packed beds at 30°C. The equilibrium selectivity was obtained as $Cr^{+3} > Mg^{2+} > Ca^{2+} \sim K^+$ for zeolite NaY and $Ca^{2+} >> Cr^{3+} > Mg^{2+} \approx K^+$ for zeolite NaX. The curves showed sequential ion exchange where $Cr^{3+}$are able to replace the competing cations. Cr^{+3} retention was investigated through a mass balance. Based on the breakthrough results, it was concluded that Cr^{+3} uptake mechanism was hardly influenced by the competition and interaction between the entering ions. NaY showed a higher affinity towards Cr^{3+} for both equilibrium and dynamic systems and its sites were more efficiently used in the ion exchange process. Cr^{3+} was less retained in NaX due to the high selectivity towards Ca^{2+}.

Covarrubias et al (2006) synthesized of modified zeolites with high Cr^{+3} exchange capacities from kaolinite and natural mordenite. The Cr^{+3} exchange capacity (CrEC) of synthesis products was determined by the type of zeolite and the fraction of amorphous phase in the solid product. It was found that the highest CrEC is obtained for synthesis products containing FAU-type zeolites. The Cr^{+3} exchange on FAU zeolites is favored due to the larger pore opening, which facilitates the diffusion of large hydrated Cr^{+3} into the internal cation exchange sites. Synthesized zeolite products presented higher Cr^{+3} exchange capacity than commercial zeolites. These results suggest that the use of these synthesized materials in Cr^{+3} removal from industrial wastewater could be promising.

Doula et al (2006) investigated the modification of natural clinoptilolite to a high surface area clinoptilolite-iron oxide system, in order to removal of Mn^{2+} from drinking water samples. The new material was obtained by adding natural clinoptilolite in $Fe(NO_3)_2$ solution under strongly basic conditions. It has specific surface area equal to 151.0 m^2/g and is fully iron exchanged (Fe/Al 1.23). Batch adsorptions were carried out to determine the effectiveness of the Clin and the Clin-Fe system in removal of manganese from drinking water. The Mn^{2+} adsorption capacity of Clin was 7.69 mg/g, whereas of Clin-Fe system was 27.12 mg/g. The main factors that contribute to difference adsorption capacity of the two solids are due to new surface species and negative charge of Clin-Fe system.

Karadag et al (2006) studied on ion exchange kinetics and equilibrium isotherms of ammonium ion (NH_4^+) on natural Turkish clinoptilolite by using a batch adsorption. The effects of some parameters such as temperature, adsorption time and initial NH_4^+ concentration were examined. The Langmuir model agrees very well with experimental data of NH_4^+ uptake. Thermodynamic parameters such as change in free energy, enthalpy and entropy were also determined. An examination of the thermodynamic parameters shows that the exchange of NH_4^+ by clinoptilolite is a process occurring spontaneously and physical in nature at ambient conditions (25 °C). The process is also found to be exothermic. The results indicate that there is a significant potential for the natural Turkish clinoptilolite as an adsorbent material for NH_4^+ removal from aqueous solutions.

Oren et al (2006) studied of factors affecting adsorption characteristics of Zn^{2+} on two natural Turkish zeolites. The results show that the Zn^{2+} adsorption behavior of both zeolites is highly dependent on the pH. Adsorption dependence on lower pH values ($pH < 4.0$) is explained by the dissolution of crystal structure and the competition of the zinc ions with the H^+. Between pH 4.0 and 6.0, the basic mechanism is the ion exchange process. Decreasing in grain size does not increase the adsorption capacity of zeolite from Gordes, yet it increases that of zeolite from Bigadic about 23%. The increasing in the initial concentration of Zn^{2+} in the system causes an increase in the adsorption capacity and then it becomes more constant at higher concentrations.

Sprynskyy et al (2006) studied the adsorption of various heavy metals (Ni^{2+}, Cu^{2+}, Pb^{2+} and Cd^{2+}) under static conditions from single component and multi component aqueous solutions by raw and pretreated clinoptilolite. It is found that finer clinoptilolite fractions adsorbed higher amounts of the metals due to relative enriching by the zeolite proper and higher cleavage. The decrease of Ni^{2+} adsorption from multicomponent solutions is probably caused by the propinquity of its sorption forms to the other metals and by competition. The maximum sorption capacity toward Cd^{2+} is determined as 4.22 mg/g at an initial concentration of 80 ppm and toward Pb^{2+}, Cu^{2+}, and Ni^{2+} as 27.7, 25.76 and 13.03 mg/g at 800 ppm. The sorption results fit well to the Langmuir and Freundlich isotherm models. The second one is better for adsorption modeling at high metal concentrations.

Urasini et al (2006) studied the cation exchange capacity (CEC) of porous zeolites allows to adsorb in the framework cavities the cations as pollutant heavy metal ions. The CEC is an useful property to create a special interface region of zeolites that if placed in the electrokinetic cell, just before the cathode, could allow to capture and concentrate the heavy metallic ions, during their migrating process. The zeolite 13X investigated in the electrokinetic proofs retains a good high ions adsorption, even if quite smaller than the relevant free solution condition and well acts as confined trap for the heavy metal ions. In fact no traces of metallic deposition are present on the electrode's surface.

Basaldella et al (2007) studied the effect of pH changes on the ability of the synthetic zeolite NaA to remove Cr^{3+} from water by ion exchange was investigated. The exchange rate was improved by working near neutrality. Despite of the occurrence of simultaneous adsorption, precipitation or cation exchange phenomena, spectroscopic analyses of samples taken at different contact times suggested the presence of a unique chromium environment in the solid phase. The increase in pH observed during the ion exchange favored polymerization-precipitation of chromium species present in solution which improved the metal removal capacity of zeolite NaA above the values expected for a pure cationic exchange reaction.

Kocaobaa, Orhanb and Akyuzc (2007) studied the removal of metal ions from aqueous solution using natural clinoptilolite under different experimental conditions. The efficiency of zeolite for the removal of Cd^{2+}, Cu^{2+} and Ni^{2+} has been determined at the different initial concentration, zeolite amount, agitation speed and pH. Adsorption data have been interpreted in terms of Langmuir and Freundlich equations. The results were provided strong support for the adsorption of heavy metals into clinoptilolite and which were found to fit sufficient by the Langmuir isotherm in the most of case. The selectivity of the studied metals was determined as $Cd^{2+} > Ni^{2+} > Cu^{2+}$.

Oztas, Karabakan and Topal (2007) investigated the Fe^{3+} adsorption from aqueous solutions onto raw and pretreated clinoptilolite. Various parameters, initial solution pH, contact time and metal ion concentration were optimized. Adsorption capacities of raw samples and those pretreated with $Na_2S_2O_8$ at 20 °C and 70 °C and with HNO_3 at 20 °C were all similar but samples pretreated with HNO_3 at 70 °C were significantly different; Fe^{3+} removal from samples pretreated with HNO_3 decreased with increasing pretreatment temperature. Tests with Fe^{3+}solutions containing phenol, CsCl or KCl, indicated the continued presence of these ions in zeolite which either promoted or retarded the adsorption of iron. The Fe^{3+}adsorption capacity of clinoptilolite pretreated with HNO_3 at 70 °C was about two times greater with, than without CsCl and KCl.

CHAPTER 3

MATERIAL AND METHODS

3.1 INSTRUMENTATION

3.1.1 Flame Atomic Absorption Spectrometer

The determinations of metal ion concentrations before and after batch adsorption by natural zeolites were performed using a Perkin-Elmer Atomic Absorption Spectrometer model AAnalyte 800, equipped with flame burner head and air/acetylene as flame. The Perkin-Elmer hollow cathode lamps were used. The instrumental parameters and flame operating conditions were listed in Table 3.1. All absorbance measurement was shown by peak height.

Table 3.1 Instrument of flame atomic absorption spectrometer operating conditions

Atomic Absorption Spectrometer operating conditions	Chromium (Cr^{3+})	Zinc (Zn^{2+})
Wavelength (nm)	357.9	213.9
Lamp current (mA)	84	40
Oxidant type	Air	Air
Oxidant flow (L/min)	17	17
Fuel type	Acetylene gas	Acetylene gas
Fuel flow (L/min)	2.5	2.5

3.1.2 pH meter

A Metrohm 713 pH meter equipped with a glass electrode, Model 6.0228.000 (Metrohm) was used for all pH measurements.

3.1.3 Analytical Balance

A Sartorius model AC 211S was used to weight natural zeolite samples throughout this work.

3.1.4 Magnetic stirrer

A JENWAY hotplate and magnetic stirrer model 1000 from United Kingdom was used for perturbation in the adsorption step.

3.2 CHEMICALS AND REAGENTS

3.2.1 Solvents

DI-water from NANOpure ultrapure water system (Dubuque, Iowa, USA) was used throughout this work.

3.2.2 Chemicals

All chemicals were atomic absorption grade which presented in Table 3.2.

Table 3.2 Chemicals and suppliers

Chemicals name	Suppliers
Chromium 1000 mg/L, Atomic Absorption Standard	SCP Science, Canada
Zinc 1000 mg/L, Atomic Absorption Standard	SCP Science, Canada
Hydrochloric acid (35.4% assay)	Carlo Erba
Sodium hydroxide (98% assay)	Carlo Erba
Natural zeolite classified as A, B, C, D, E, F and G	Songkhla province, Thailand

3.3 NATURAL ZEOLITES AS ADSORBENT MATERIALS

7 natural zeolites used were obtained from Songkhla province, the south of Thailand. The information of 7 natural zeolites such as name, phase type, chemical formula and number of impurity was presented in Table 3.3 (Santhong., 2007).

Table 3.3 The structural characterization information of 7 natural zeolites

Classified name	Phase type	Chemical formula	Impurity
A	Mordenite	$(Na_2, Ca, K_2)Al_2Si_{10}O_{24}.7H_2O$	Sodium Iron Silicon oxide Hydrate α-Quartz
B	Kaolinite	$Al_4(Si_4O_{10})(OH)_8$	Quartz
C	Kaolinite 1Md	$Al_2(Si_2O_5)(OH)_4$	Quartz
D	Kaolinite	$Al_2(Si_2O_5)(OH)_4$	α-Quartz
E	Clinoptilolite	$(Na, Ca, K)_{2.5}Al_3(Al, Si)_2Si_{13}O_{36}$	Gypsum
F	Clinoptilolite	$(Na, Ca, K)_{2.5}Al_3(Al, Si)_2Si_{13}O_{36}$	Gypsum
G	Clinoptilolite	$(Na, Ca, K)_{2.5}Al_3(Al, Si)_2Si_{13}O_{36}$	Gypsum

The structural characterization information of 7 natural zeolites was obtained from the Special project of Miss.Anchana Santhong from department of physics, faculty of science, Ubon Rajathanee University. The results derived from X-ray diffraction and X-ray florescence techniques were showed.

3.4 PREPARATION OF SOLUTION

3.4.1 Standard Chromium (III) Solution and Calibration Curve

1) Dilution of stock standard 1000.00 ppm Cr^{3+} solution in the volume of 25.00, 50.00, 75.00, 100.00 and 125.00 μL was performed by diluting to volume of 25.00 ml with DI-water in 5 bottles of 25 ml volumetric flask. Then a 1.00, 2.00, 3.00, 4.00 and 5.00 ppm standard Cr^{3+} solution were obtained.

2) Absorbance of all standard Cr^{3+} solution was measured by using atomic absorption spectrophotometer at wavelength of 357.9 nm. DI-water was used as blank.

3) Calibration curve of standard Cr^{3+} solution was performed by plotting entire standard Cr^{3+} concentration as X-axis against their absorbance value as Y-axis.

3.4.2 Standard Zinc (II) Solution and Calibration Curve

1) Dilution of stock standard 1000.00 ppm Zn^{2+} solution in the volume of 6.25, 12.50, 18.75 and 25.00 μL was performed by diluting to volume of 25.00 ml with DI-water in 4 bottles of 25 ml volumetric flask. Then a 0.25, 0.50, 0.75 and 1.00 ppm standard Zn^{2+} solution were obtained.

2) Absorbance of all standard Zn^{2+} solution was measured by using atomic absorption spectrophotometer at wavelength of 213.9 nm. DI-water was used as blank.

3) Calibration curve of standard Zn^{2+} solution was performed by plotting entire standard Zn^{2+} concentration as X-axis against their absorbance value as Y-axis.

3.5 PRELIMINARY ADSORPTION STUDY BY USING 7 NATURAL ZEOLITES

3.5.1 Procedure for preliminary chromium (III) adsorption

3.5.1.1 Determination of Cr^{3+} concentration before batch adsorption

1) 10.00 ppm Cr^{3+} working solution was prepared by accurately diluting 20.00 ml of stock standard 1000.00 ppm Cr^{3+} in 2000 ml volumetric flask. Then, working solution was obtained by adding up DI-water to 2000.00 ml.

2) Absorbance of Cr^{3+} working solution was measured by using atomic absorption spectrophotometer at wavelength of 357.9 nm. DI-water was used as blank.

3) Concentration of Cr^{3+} working solution was calculated by using linear equation from Cr^{3+} calibration curve.

3.5.1.2 Determination of Cr^{3+} concentration after batch adsorption

1) Each of weighed 7 natural zeolites (2.0 g) was put into 4 bottles of 250 ml Erlenmeyer flask with 50.00 ml of 10.00 ppm Cr^{3+} working solution. The first bottle was used as reagent blank.

2) All suspensions were performed batch adsorption for an hour. Systematic perturbation was performed by using magnetic stirrer at the time of 30 minutes for a half minute.

3) All solutions were kept in Nalgene bottle after filtration of all suspension through Whatman filter paper no.1.

4) Concentration of Cr^{3+} after batch adsorption was measured by using atomic absorption spectrophotometer at wavelength of 357.9 nm.

3.5.2 Procedure for preliminary zinc (II) adsorption

3.5.2.1 Determination of Zn^{2+} concentration before batch adsorption

1) 10.00 ppm Zn^{2+} working solution was prepared by accurately diluting 20.00 ml of stock standard 1000.00 ppm Zn^{2+} in 2000 ml volumetric flask. Then, working solution was obtained by adding up DI-water to 2000.00 ml.

2) Absorbance of Zn^{2+} working solution was measured by using atomic absorption spectrophotometer at wavelength of 213.9 nm. DI-water was used as blank.

3) Concentration of Zn^{2+} working solution was calculated by using linear equation from Zn^{2+} calibration curve.

3.5.2.2 Determination of Zn^{2+} concentration after batch adsorption

1) Each of weighed 7 natural zeolites (2.0 g) was put into 4 bottles of 250 ml Erlenmeyer flask with 50.00 ml of 10.00 ppm Zn^{2+} working solution. The first bottle was used as reagent blank.

2) All suspensions were performed batch adsorption for an hour. Systematic perturbation was performed by using magnetic stirrer at the time of 30 minutes for a half minute.

3) All solutions were kept in Nalgene bottle after filtration of all suspension through Whatman filter paper no.1.

4) Concentration of Zn^{2+} after batch adsorption was measured by using atomic absorption spectrophotometer at wavelength o f 213.9 nm.

3.6 INVESTIGATION OF OPTIMUM CONDITION FOR ADSORPTION OF METAL IONS BY NATURAL ZEOLITES

3.6.1 Effect of zeolite amount on optimum adsorption of metal ions

3.6.1.1 Adsorption of chromium (III)

1) Determination of Cr^{3+} concentration before batch adsorption

1.1) 10.00 ppm Cr^{3+} working solution was prepared by accurately diluting 20.00 ml of stock standard 1000.00 ppm Cr^{3+} in 2000 ml volumetric flask. Then, working solution was obtained by adding up DI-water to 2000.00 ml.

1.2) Absorbance of Cr^{3+} working solution was measured by using atomic absorption spectrophotometer at wavelength of 357.9 nm. DI-water was used as blank.

1.3) Concentration of Cr^{3+} working solution was calculated by using linear equation from Cr^{3+} calibration curve.

2) Determination of Cr^{3+} concentration after batch adsorption

2.1) 4 natural zeolites given the best result from the preliminary adsorption of Cr^{3+} were selected.

2.2) Each of 4 natural zeolites was accurately weighed and put into 60 bottles of 250 ml Erlenmeyer flask. The zeolite amounts were shown in Table 3.4 below;

Table 3.4 Effect of zeolite amount on Cr^{3+} adsorption

Experimental time	Amount of zeolite (g)	Experimental description	
		Replication (flask)	Reagent blank (flask no.)
1	1.0	4	1
2	1.5	4	1
3	2.0	4	1
4	2.5	4	1
5	3.0	4	1

2.3) 50.00 ml of 10.00 ppm Cr^{3+} working solution was added into all above Erlenmeyer flasks. Then batch adsorption was performed by suspending all natural zeolites in Cr^{3+} working solution for an hour. Systematic perturbation was performed by using magnetic stirrer at the time of 30 minutes for a 30 second.

2.4) All solutions were kept in Nalgene bottle after filtration of all suspension through Whatman filter paper no.1.

2.5) Concentration of Cr^{3+} after batch adsorption was measured by using atomic absorption spectrophotometer at wavelength of 357.9 nm.

3.6.1.2 Adsorption of zinc (II)

1) Determination of Zn^{2+} concentration before batch adsorption

1.1) 10.00 ppm Zn^{2+} working solution was prepared by accurately diluting 20.00 ml of stock standard 1000.00 ppm Zn^{2+} in 2000 ml volumetric flask. Then, working solution was obtained by adding up DI-water to 2000.00 ml.

1.2) Absorbance of Zn^{2+} working solution was measured by using atomic absorption spectrophotometer at wavelength of 213.9 nm. DI-water was used as blank.

1.3) Concentration of Zn^{2+} working solution was calculated by using linear equation from Zn^{2+} calibration curve.

2) Determination of Zn^{2+} concentration after batch adsorption

2.1) 4 natural zeolites given the best result from the preliminary adsorption of Zn^{2+} were selected.

2.2) Each of 4 natural zeolites was accurately weighed and put into 60 bottles of 250 ml Erlenmeyer flask. The zeolite amounts were shown in Table 3.5 below;

Table 3.5 Effect of zeolite amount on Zn^{2+} adsorption

Experimental time	Amount of zeolite (g)	Experimental description	
		Replication (flask)	Reagent blank (flask no.)
1	1.0	4	1
2	1.5	4	1
3	2.0	4	1
4	2.5	4	1
5	3.0	4	1

2.3) 50.00 ml of 10.00 ppm Zn^{2+} working solution was added into all above Erlenmeyer flasks. Then batch adsorption was performed by suspending all natural zeolites in Zn^{2+} working solution for an hour. Systematic perturbation was performed by using magnetic stirrer at the time of 30 minutes for a 30 second.

2.4) All solutions were kept in Nalgene bottle after filtration of all suspension through Whatman filter paper no.1.

2.5) Concentration of Zn^{2+} after batch adsorption was measured by using atomic absorption spectrophotometer at wavelength of 213.9 nm.

3.6.2 Effect of adsorption time on optimum adsorption of metal ions

3.6.2.1 Adsorption of chromium (III)

1) Determination of Cr^{3+} concentration before batch adsorption

1.1) 10.00 ppm Cr^{3+} working solution was prepared by accurately diluting 20.00 ml of stock standard 1000.00 ppm Cr^{3+} in 2000 ml volumetric flask. Then, working solution was obtained by adding up DI-water to 2000.00 ml.

1.2) Absorbance of Cr^{3+} working solution was measured by using atomic absorption spectrophotometer at wavelength of 357.9 nm. DI-water was used as blank.

1.3) Concentration of Cr^{3+} working solution was calculated by using linear equation from Cr^{3+} calibration curve.

2) Determination of Cr^{3+} concentration after batch adsorption

2.1) Each of 4 natural zeolites was accurately weighed in the optimum amount and put into 60 bottles of 250 ml Erlenmeyer flask.

2.2) 50.00 ml of 10.00 ppm Cr^{3+} working solution was added into all above Erlenmeyer flasks.

2.3) Batch adsorption was performed by suspending all natural zeolites in Cr^{3+} working solution. Effect of adsorption time was performed by the Table 3.6 below;

Table 3.6 Effect of adsorption time on Cr^{3+} adsorption

Experimental time	Adsorption time (hrs.)	Perturbation time (at the hour of)	Experimental description	
			Replication (flask)	Reagent blank (flask No.)
1	1	½	4	1
2	2	1	4	1
3	6	3	4	1
4	12	6	4	1
5	24	12	4	1

Systematic perturbation was performed by using magnetic stirrer at the half time adsorption for a 30 second.

2.4) All solutions were kept in Nalgene bottle after filtration of all suspension through Whatman filter paper no.1.

2.5) Concentration of Cr^{3+} after batch adsorption was measured by using atomic absorption spectrophotometer at wavelength of 357.9 nm.

3.6.2.2 Adsorption of zinc (II)

1) Determination of Zn^{2+} concentration before batch adsorption

1.1) 10.00 ppm Zn^{2+} working solution was prepared by accurately diluting 20.00 ml of stock standard 1000.00 ppm Zn^{2+} in 2000 ml volumetric flask. Then, working solution was obtained by adding up DI-water to 2000.00 ml.

1.2) Absorbance of Zn^{2+} working solution was measured by using atomic absorption spectrophotometer at wavelength of 213.9 nm. DI-water was used as blank.

1.3) Concentration of Zn^{2+} working solution was calculated by using linear equation from Zn^{2+} calibration curve.

2) Determination of Zn^{2+} concentration after batch adsorption

2.1) Each of 4 natural zeolites was accurately weighed in the optimum amount and put into 60 bottles of 250 ml Erlenmeyer flask.

2.2) 50.00 ml of 10.00 ppm Zn^{2+} working solution was added into all above Erlenmeyer flasks.

2.3) Batch adsorption was performed by suspending all natural zeolites in Zn^{2+} working solution. Effect of adsorption time was performed by the Table 3.7 below;

Table 3.7 Effect of adsorption time on Zn^{2+} adsorption

Experimental time	Adsorption time (hrs.)	Perturbation time (at the hour of)	Experimental description	
			Replication (flask)	Reagent blank (flask No.)
1	1	½	4	1
2	2	1	4	1
3	6	3	4	1
4	12	6	4	1
5	24	12	4	1

Systematic perturbation was performed by using magnetic stirrer at the half time adsorption for a 30 second.

2.4) All solutions were kept in Nalgene bottle after filtration of all suspension through Whatman filter paper no.1.

2.5) Concentration of Zn^{2+} after batch adsorption was measured by using atomic absorption spectrophotometer at wavelength of 213.9 nm.

3.6.3 Effect of initial solution pH on optimum adsorption of metal ions

3.6.3.1 Adsorption of chromium (III)

1) Determination of Cr^{3+} concentration before batch adsorption

1.1) 10.00 ppm Cr^{3+} working solution was prepared by accurately diluting 20.00 ml of stock standard 1000.00 ppm Cr^{3+} in 2000 ml volumetric flask. Then, working solution was obtained by adding up DI-water to 2000.00 ml.

1.2) The initial pH of working Cr^{3+} solution was measured by using pH meter and adjusted by using 0.10 M HCl or 0.10 M NaOH for uptake the initial pH solution of 3.0, 5.0, 7.0, 9.0 and 11.0.

1.3) Absorbance of Cr^{3+} working solution was measured by using atomic absorption spectrophotometer at wavelength of 357.9 nm. DI-water was used as blank.

1.4) Concentration of Cr^{3+} working solution was calculated by using linear equation from Cr^{3+} calibration curve.

2) Determination of Cr^{3+} concentration after batch adsorption

2.1) Each of 4 natural zeolites was accurately weighed in the optimum amount and put into 60 bottles of 250 ml Erlenmeyer flask.

2.2) 50.00 ml of 10.00 ppm Cr^{3+} working solution was added into all above Erlenmeyer flasks. Effect of initial solution pH was performed by the Table 3.8 below;

Table 3.8 Effect of initial solution pH on Cr^{3+} adsorption

Experimental time	Initial solution pH	Experimental description	
		Replication (flask)	Reagent blank (flask no.)
1	3.0	4	1
2	5.0	4	1
3	7.0	4	1
4	9.0	4	1
5	11.0	4	1

2.3) Batch adsorption was performed by suspending all natural zeolites in Cr^{3+} working solution for an optimum adsorption time. Systematic perturbation was performed by using magnetic stirrer at the half time adsorption for a 30 second.

2.4) All solutions were kept in Nalgene bottle after filtration of all suspension through Whatman filter paper no.1.

2.5) Concentration of Cr^{3+} after batch adsorption was measured by using atomic absorption spectrophotometer at wavelength of 357.9 nm.

3.6.3.2 Adsorption of zinc (II)

1) Determination of Zn^{2+} concentration before batch adsorption

1.1) 10.00 ppm Zn^{2+} working solution was prepared by accurately diluting 20.00 ml of stock standard 1000.00 ppm Zn^{2+} in 2000 ml volumetric flask. Then, working solution was obtained by adding up DI-water to 2000.00 ml.

1.2) The initial pH of working Zn^{2+} solution was measured by using pH meter and adjusted by using 0.10 M HCl or 0.10 M NaOH for uptake the initial pH solution of 3.0, 5.0, 7.0, 9.0 and 11.0.

1.3) Absorbance of Zn^{2+} working solution was measured by using atomic absorption spectrophotometer at wavelength of 213.9 nm. DI-water was used as blank.

1.4) Concentration of Zn^{2+} working solution was calculated by using linear equation from Zn^{2+} calibration curve.

2) Determination of Zn^{2+} concentration after batch adsorption

2.1) Each of 4 natural zeolites was accurately weighed in the optimum amount and put into 60 bottles of 250 ml Erlenmeyer flask.

2.2) 50.00 ml of 10.00 ppm Zn^{2+} working solution was added into all above Erlenmeyer flasks. Effect of initial solution pH was performed by the Table 3.9 below;

Table 3.9 Effect of initial solution pH on Zn^{2+} adsorption

Experimental time	Initial solution pH	Experimental description	
		Replication (flask)	Reagent blank (flask no.)
1	3.0	4	1
2	5.0	4	1
3	7.0	4	1
4	9.0	4	1
5	11.0	4	1

2.3) Batch adsorption was performed by suspending all natural zeolites in Zn^{2+} working solution for an optimum adsorption time. Systematic perturbation was performed by using magnetic stirrer at the half time adsorption for a 30 second.

2.4) All solutions were kept in Nalgene bottle after filtration of all suspension through Whatman filter paper no.1.

2.5) Concentration of Zn^{2+} after batch adsorption was measured by using atomic absorption spectrophotometer at wavelength of 213.9 nm.

3.6.4 Effect of initial metal ion concentration on optimum adsorption of metal ions

3.6.4.1 Adsorption of chromium (III)

1) Determination of Cr^{3+} concentration before batch adsorption

1.1) 5.00, 10.00, 20.00 and 30.00 ppm Cr^{3+} working solution was prepared by accurately diluting 2.50, 5.00, 10.00 and 20.00 ml of stock standard 1000.00 ppm Cr^{3+}

in each 500 ml volumetric flask. Then, all working solution was obtained by adding up DI-water to 500.00 ml.

1.2) The initial pH of Cr^{3+} working solution was measured by using pH meter and adjusted by using 0.10 M HCl or 0.10 M NaOH for uptake the initial pH solution of 3.0, 5.0, 7.0, 9.0 and 11.0.

1.3) Absorbance of Cr^{3+} working solution was measured by using atomic absorption spectrophotometer at wavelength of 357.9 nm. DI-water was used as blank.

1.4) Concentration of Cr^{3+} working solution was calculated by using linear equation from Cr^{3+} calibration curve.

2) Determination of Cr^{3+} concentration after batch adsorption

2.1) Each of 4 natural zeolites was accurately weighed in the optimum amount and put into 48 bottles of 250 ml Erlenmeyer flask.

2.2) 50.00 ml of entire Cr^{3+} working solution was added into all above Erlenmeyer flasks. Effect of initial Cr^{3+} concentration was performed by the Table 3.10 below;

Table 3.10 Effect of initial Cr^{3+} concentration on chromium adsorption

Experimental time	Initial Cr^{3+} concentration (ppm)	Experimental description	
		Replication (flask)	Reagent blank (flask no.)
1	5.00	4	1
2	10.00	4	1
3	20.00	4	1
4	30.00	4	1

2.3) Batch adsorption was performed by suspending all natural zeolites in Cr^{3+} working solution. Systematic perturbation was performed by using magnetic stirrer at the half time adsorption for a 30 second.

2.4) All solutions were kept in Nalgene bottle after filtration of all suspension through Whatman filter paper no.1.

2.5) Concentration of Cr^{3+} after batch adsorption was measured by using atomic absorption spectrophotometer at wavelength of 357.9 nm.

3.6.4.2 Adsorption of zinc (II)

1) Determination of Zn^{2+} concentration before batch adsorption

1.1) 5.00, 10.00, 20.00 and 30.00 ppm Zn^{2+} working solution was prepared by accurately diluting 2.50, 5.00, 10.00 and 20.00 ml of stock standard 1000.00 ppm Zn^{2+} in each 500 ml volumetric flask. Then, all working solution was obtained by adding up DI-water to 500.00 ml.

1.2) The initial pH of Zn^{2+} working solution was measured by using pH meter and adjusted by using 0.10 M HCl or 0.10 M NaOH for uptake the initial pH solution of 3.0, 5.0, 7.0, 9.0 and 11.0.

1.3) Absorbance of Zn^{2+} working solution was measured by using atomic absorption spectrophotometer at wavelength of 213.9 nm. DI-water was used as blank.

1.4) Concentration of Zn^{2+} working solution was calculated by using linear equation from Zn^{2+} calibration curve.

2) Determination of Zn^{2+} concentration after batch adsorption

2.1) Each of 4 natural zeolites was accurately weighed in the optimum amount and put into 48 bottles of 250 ml Erlenmeyer flask.

2.2) 50.00 ml of entire Zn^{2+} working solution was added into all above Erlenmeyer flasks. Effect of initial Zn^{2+} concentration was performed by the Table 3.11 below;

Table 3.11 Effect of initial Zn^{2+} concentration on chromium adsorption

Experimental time	Initial Zn^{2+} concentration (ppm)	Experimental description	
		Replication (flask)	Reagent blank (flask no.)
1	5.00	4	1
2	10.00	4	1
3	20.00	4	1
4	30.00	4	1

2.3) Batch adsorption was performed by suspending all natural zeolites in Zn^{2+} working solution. Systematic perturbation was performed by using magnetic stirrer at the half time adsorption for a 30 second.

2.4) All solutions were kept in Nalgene bottle after filtration of all suspension through Whatman filter paper no.1.

2.5) Concentration of Zn^{2+} after batch adsorption was measured by using atomic absorption spectrophotometer at wavelength of 213.9 nm.

3.7 INVESTIGATION OF ADSORPTION ISOTHERMS

3.7.1 Freundlich isotherm

3.7.1.1 Freundlich isotherm for adsorption of chromium (III)

1) Freundlich isotherm for Cr^{3+} adsorption was obtained by plotting the value of log C_e as X-axis against log C_{ads} as Y-axis over entire concentration range of Cr^{3+} ions. The Freundlich isotherm equation is as following;

$$\log C_{ads} = 1/n \log C_e + \log K$$

Where;	C_e	is	the equilibrium concentration of Cr^{3+} ions in solution
	C_{ads}	is	the concentration of Cr^{3+} ions adsorbed onto zeolite
	K	is	a parameter related to the temperature
	n	is	a characteristic constant for the adsorption system under study

2) The Freundlich constants (n and K) were calculated from slope and intercept from linear equation.

3) The obtained Freundlich constants (K and n) were compared with experimental results from preliminary adsorption for checking of the accuracy and consistency between them. R^2 of all linear equation were considered the reasonable of isotherm model.

3.7.1.2 Freundlich isotherm for adsorption of zinc (II)

1) Freundlich isotherm for Zn^{2+} adsorption was obtained by plotting the value of log C_e as X-axis against log C_{ads} as Y-axis over entire concentration range of Zn^{2+} ions. The Freundlich isotherm equation is as following;

$$\log C_{ads} = 1/n \log C_e + \log K$$

Where; C_e is the equilibrium concentration of Zn^{2+} ions in solution

C_{ads} is the concentration of Zn^{2+} ions adsorbed onto zeolite

K is a parameter related to the temperature

n is a characteristic constant for the adsorption system under study

2) The Freundlich constants (n and K) were calculated from slope and intercept from linear equation.

3) The obtained Freundlich constants (K and n) were compared with experimental results from preliminary adsorption for checking of the accuracy and consistency between them. The correlation coefficient, R^2, of all linear equation were use to consider for the reasonable isotherm model.

3.7.2 Langmuir isotherm

3.7.2.1 Langmuir isotherm for adsorption of chromium (III)

1) Langmuir isotherm for Cr^{3+} adsorption was obtained by plotting the value of C_e as X-axis against C_e/C_{ads} as Y-axis over entire concentration range of Cr^{3+} ions. The Langmuir isotherm equation is as following;

$$C_e/C_{ads} = C_e/Q + 1/Qb$$

Where; C_e is the equilibrium concentration of Cr^{3+} ions in solution

C_{ads} is the concentration of Cr^{3+} ions adsorbed onto zeolite

Q is Langmuir constants related to sorption capacity

b is Langmuir constants related to sorption energy

2) The Langmuir constants (Q and b) were calculated from slope and intercept from linear equation.

3) The obtained Langmuir constants (Q and b) were compared with experimental results from preliminary adsorption for checking of the accuracy and consistency between them. R^2 of all linear equation were considered the reasonable of isotherm model.

3.7.2.2 Langmuir isotherm for adsorption of zinc (II)

1) Langmuir isotherm for Zn^{2+} adsorption was obtained by plotting the value of C_e as X-axis against C_e/C_{ads} as Y-axis over entire concentration range of Zn^{2+} ions. The Langmuir isotherm equation is as following;

$$C_e/C_{ads} = C_e/Q + 1/Qb$$

Where;			
	C_e	is	the equilibrium concentration of Zn^{2+} ions in solution
	C_{ads}	is	the concentration of Zn^{2+} ions adsorbed onto zeolite
	Q	is	Langmuir constants related to sorption capacity
	b	is	Langmuir constants related to sorption energy

2) The Langmuir constants (Q and b) were calculated from slope and intercept from linear equation.

3) The obtained Langmuir constants (Q and b) were compared with experimental results from preliminary adsorption for checking of the accuracy and consistency between them. R^2 of all linear equation were considered the reasonable of isotherm model.

CHAPTER 4

RESULTS AND DISCUSSION

Preliminary adsorption study of chromium (III) and zinc (II) ions from aqueous solution in laboratory scale using 7 natural zeolites from Songkhla province were firstly performed. The natural zeolites showing high efficiency of chromium and zinc removal were selected for further study. Effect of zeolites amount, adsorption time, initial solution pH and initial metal ion concentration were then investigated to obtain the optimum condition for removal of chromium and zinc ions from aqueous solution. In the final part, to explain the interaction and behavior of metal ions on surface of natural zeolites as adsorbent, concentration of metal ions over the entire concentration range of all metal ions was used to study the adsorption isotherm.

4.1 PRELIMINARY ADSORPTION STUDY BY USING 7 NATURAL ZEOLITES

Batch adsorption is used to remove chromium and zinc ions by using 7 natural zeolites classified as A, B, C, D, E, F and G. For the condition used in the preliminary study, 40 g/l of each natural zeolite were suspended in 10.00 ppm metal ion solution for an hour. The aim of this part is to study on the removal efficiency and the feasibility of using natural zeolites as adsorbent material for removal of heavy metal in prepared aqueous solution. The result of preliminary adsorptions study is showed in Table 4.1. The concentration of chromium and zinc after batch experiment was measured by using atomic absorption spectrophotometer at wavelengths of 357.9 nm. and 213.9 nm. for chromium and zinc, respectively.

Table 4.1 Preliminary adsorption study of chromium and zinc by using 7 natural zeolites[1]

Classified natural zeolites	Average chromium adsorption		Average zinc adsorption	
	Chromium adsorbed (ppm)[2]	Adsorption efficiency (%)	Zinc adsorbed (ppm)[3]	Adsorption efficiency (%)
A	10.255 (± 0.008)	95.06	8.441 (± 0.005)	82.38
B	10.003 (± 0.009)	92.73	5.926 (± 0.005)	57.84
C	9.590 (± 0.005)	88.90	4.938 (± 0.006)	48.19
D	9.977 (± 0.004)	92.49	6.224 (± 0.004)	60.75
E	7.408 (± 0.008)	68.67	1.734 (± 0.003)	16.90
F	7.143 (± 0.010)	66.21	1.718 (± 0.008)	16.77
G	5.536 (± 0.005)	51.31	1.702 (± 0.006)	16.61

[1] Initial Cr^{3+} and Zn^{2+} concentrations are 10.788 and 10.246 ppm, respectively. 3 replicate adsorptions are performed

[2, 3] The SD of each average adsorbed concentration is the number in parentheses.

The term of adsorption efficiency or removal efficiency is used to indicate the efficiency of natural zeolites which are used as adsorbent material to adsorb or remove some metal ions in aqueous solution. It can be calculated as a function of the initial concentration and equilibrate concentration. The adsorption efficiency is defined as:

$$Adsorption\ efficiency = \frac{C_i - C_e}{C_i} x\, 100 = \frac{C_{ads}}{C_i} x\, 100$$

Where; C_i is the initial metal ions concentration

C_e is the equilibrium metal ions concentration in aqueous solution

C_{ads} is the concentration of chromium ions adsorbed onto zeolite

In Table 4.1, the results show an average chromium ion adsorption efficiency of 95.06%, 92.73%, 88.90%, 92.49%, 68.67%, 62.21% and 51.31% for zeolites A, B, C, D, E, F and G, respectively. For zinc removal, an average zinc ion adsorption efficiency is 82.38%, 57.84%, 48.19%, 60.75%, 16.90%, 16.77% and 16.61% for zeolites A, B, C, D, E, F and G, respectively.

It is observed that the adsorption efficiency of chromium and zinc for natural zeolites A-D is higher than zeolites E-G.

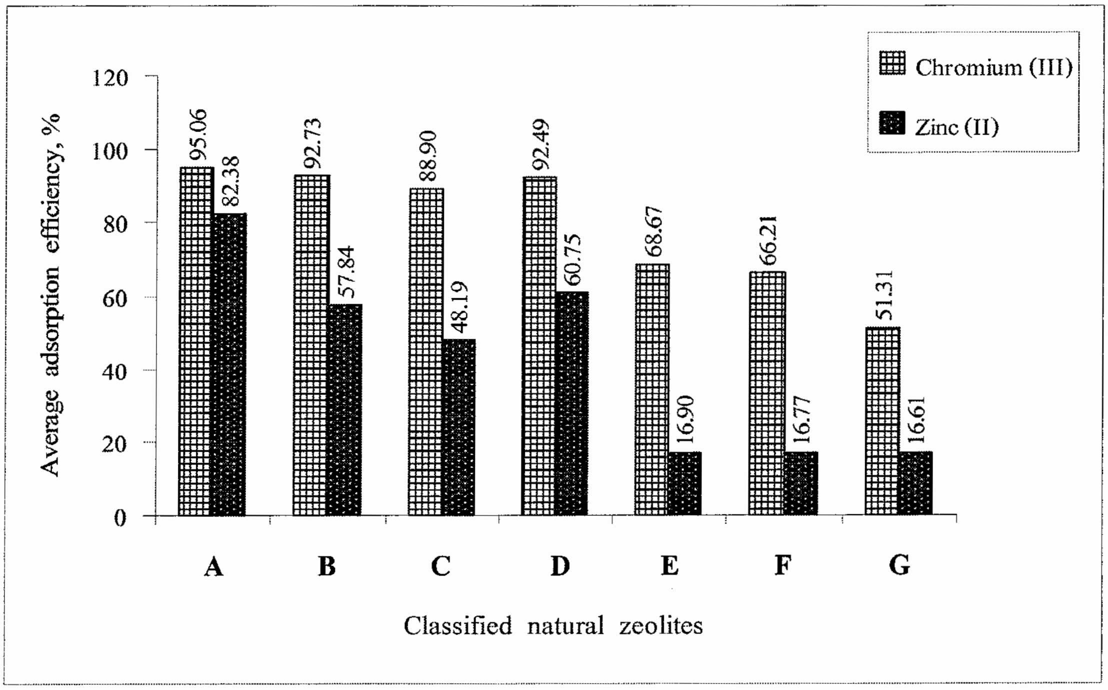

Figure 4.1 Comparison of adsorption efficiency of chromium and zinc by 7 natural zeolites on Preliminary adsorption study

Figure 4.1 shows the comparison of adsorption efficiency of chromium and zinc by using 7 natural zeolites in the preliminary adsorption study. It is found that the adsorption efficiency of zinc is lower than chromium. Chromium ion forms the octahedral complex ions surrounding with six water molecules in the solution. While, zinc ion forms the tetrahedral complex ions surrounding with four water molecules in the solution (Phasookkavanich., 1999). The complex ions will pass through the channel, pore and cage of zeolite in these forms. The electrostatic interaction between positive charge of hydrated metal complexes and negative charge of zeolite surfaces is then occurred. When hydrated metal complexes are contacting to zeolite surface, water molecules will be stripped out from the solvated ions. Only metal ions are adsorbed onto zeolite surface. The adsorbed phenomena depends on the charge density of cations, columbic interaction between metal ions and active sites on zeolite surfaces, the diameter of hydrate metal complex, size of internal pore, channel and cage of zeolite and number of active sites on surface of zeolites (Erdem, Karapinar and Donat., 2004).

In this work, preparation of metal ions was performed by using standard chromium and zinc for atomic absorption grade which is contained only Cr^{+3} and Zn^{+2}, respectively. An ionic radius of Cr^{+3} is 64 pm. which is smaller than Zn^{+2} (74 pm.) (Chang., 1994). Then, the uptake of Cr^{+3} (the smaller diameter) has maximum adsorption efficiency which is larger than Zn^{+2} (the bigger diameter).

4.2 INVESTIGATION OF OPTIMUM CONDITION FOR REMOVAL OF METAL IONS BY NATURAL ZEOLITES

This result is the second part of the application of natural zeolites for removal of chromium and zinc ion from prepared aqueous solution in laboratory scale. The following parameters were selected to study the optimum condition.

- Effect of zeolite amount
- Effect of adsorption time
- Effect of initial solution pH
- Effect of initial metal ion concentration

According to Table 4.1, from preliminary adsorption study, the results show 4 natural zeolites classified as A, B, C and D given highest adsorption efficiency of both studied metals. There are more than 85% and 60% for removal of chromium and zinc from solution, respectively. Then, 4 natural zeolites classified as A, B, C and D were selected to further study.

4.2.1 Effect of zeolite amount

The effect of zeolite amount on adsorption of chromium and zinc was studied in order to ensure that adsorption efficiency depends on number of active site on natural zeolite surface. Zeolite amount is representing to the number of active site reacting with positive charge of metal cations.

Study of the effect of zeolite amount was performed by varying 4 natural zeolites from 1.00, 1.50, 2.00, 2.50 and 3.00 g. The results of adsorbed metal ion concentration are presented in Table 4.2.

Table 4.2 Effect of zeolite amount on chromium and zinc ions adsorption[1]

Metal ion	Zeolite amount (g)	Adsorbed concentration (ppm)[2] A	B	C	D
Cr^{3+}	1.0	9.361 (± 0.005)	7.092 (± 0.005)	6.440 (± 0.008)	7.217 (± 0.004)
	1.5	9.384 (± 0.008)	8.659 (± 0.007)	8.270 (± 0.008)	8.661 (± 0.004)
	2.0	9.393 (± 0.004)	9.125 (± 0.004)	8.609 (± 0.007)	8.937 (± 0.005)
	2.5	9.359 (± 0.005)	9.228 (± 0.005)	8.871 (± 0.006)	9.012 (± 0.008)
	3.0	9.381 (± 0.005)	9.234 (± 0.004)	8.991 (± 0.004)	9.041 (± 0.004)
Zn^{2+}	1.0	4.816 (± 0.012)	4.330 (± 0.012)	3.355 (± 0.005)	4.253 (± 0.005)
	1.5	5.736 (± 0.005)	5.100 (± 0.005)	3.885 (± 0.008)	4.935 (± 0.005)
	2.0	6.556 (± 0.008)	5.373 (± 0.005)	4.440 (± 0.012)	5.345 (± 0.008)
	2.5	7.328 (± 0.003)	5.255 (± 0.005)	4.728 (± 0.003)	5.785 (± 0.008)
	3.0	7.754 (± 0.006)	5.798 (± 0.008)	4.890 (± 0.005)	5.933 (± 0.005)

[1] Initial Cr^{3+} and Zn^{2+} concentrations are 9.696 and 9.220 ppm, respectively at pH 7.00. 3 replicate adsorptions are performed.

[2] The SD of each average adsorbed concentration is the number in parentheses.

The adsorption efficiency of the effect of zeolite amount was calculated and presented in Table 4.3.

Table 4.3 Effect of zeolite amount on adsorption efficiency[1]

Metal ion	Zeolite amount (g)	Adsorption efficiency (%) A	B	C	D
Cr^{3+}	1.0	96.55	73.14	66.41	74.43
	1.5	96.78	89.30	85.29	89.33
	2.0	96.87	94.11	88.79	92.17
	2.5	96.52	95.17	91.49	92.95
	3.0	96.75	95.23	92.72	93.25

Table 4.3 Effect of zeolite amount on adsorption efficiency[1] (continued)

Metal ion	Zeolite amount (g)	Adsorption efficiency (%)			
		A	B	C	D
Zn^{2+}	1.0	49.67	44.66	34.60	43.86
	1.5	59.16	52.60	40.07	50.90
	2.0	67.62	55.41	45.79	55.13
	2.5	75.58	54.20	48.76	59.66
	3.0	79.97	59.79	50.43	61.19

The relationship between adsorption efficiency and amount of natural zeolite for chromium and zinc adsorption is showed in Figures 4.2 and 4.3, respectively.

Figure 4.2 shows 1.0 g of zeolite A in 50.00 ml of 10.00 ppm chromium working solution is an optimum amount for the removal of chromium. For zeolites B, C and D, 1.5 g is an optimum amount for the adsorption of chromium.

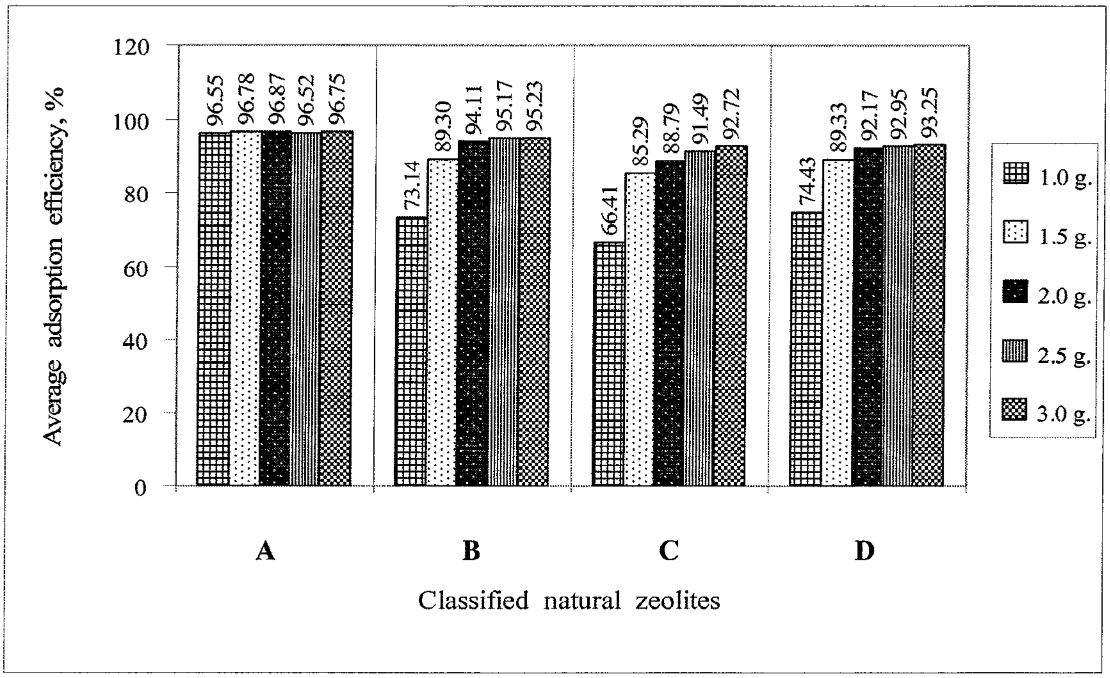

Figure 4.2 Comparison of adsorption efficiency of chromium by 4 natural zeolites on the effect of zeolite amount

From Figure 4.3, 1.5 g of zeolites A, B, C and D is an optimum amount for the removal of zinc in 50.00 ml of 10.00 ppm zinc working solution.

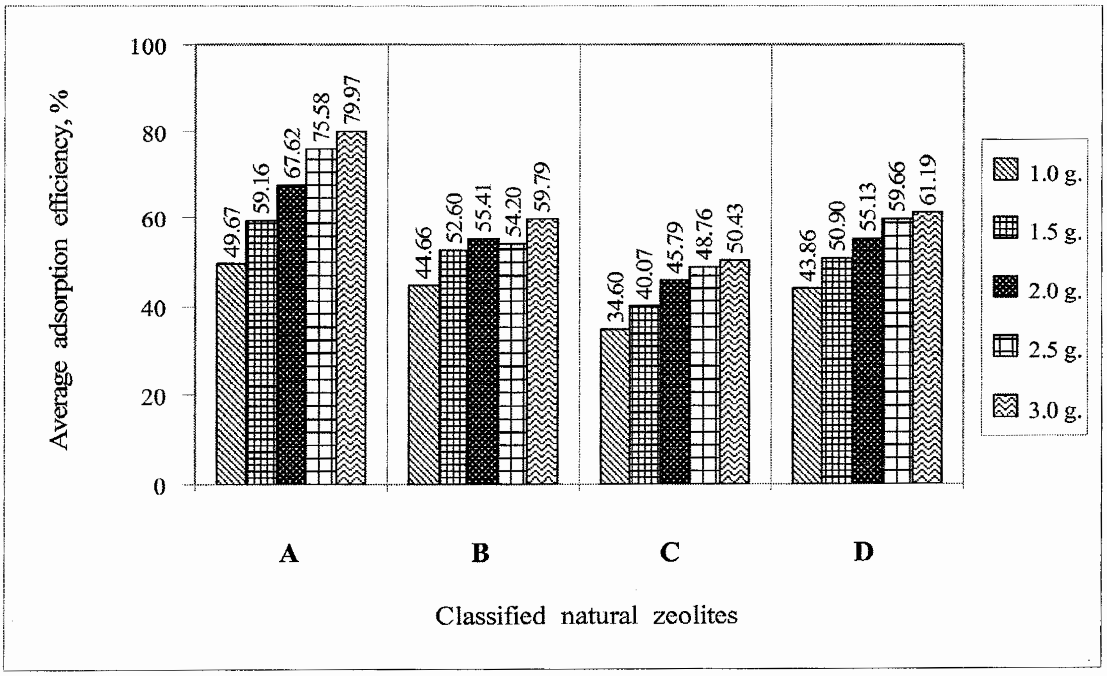

Figure 4.3 Comparison of adsorption efficiency of Zinc by 4 natural zeolites on the effect of zeolite amount

When compared the adsorption efficiency between chromium and zinc, it is consistent to the results of the preliminary study that adsorption efficiency of chromium is higher than zinc. Adsorption efficiency dramatically increases with increasing zeolite amount. Increasing in zeolite amount is attributed to increase in the specific surface area and number of active site.

4.2.2 Effect of adsorption time

It is necessary to know the optimum adsorption time to obtain maximum adsorption of metal ions on natural zeolites. The effect of adsorption time was studied by varying the adsorption time from 1, 2, 6, 12 and 24 hours. Systematic perturbation was carried out by magnetic stirrer at the time of 1/2, 1, 3, 6 and 12 hours, respectively, for 30 seconds. The results of adsorbed metal ion concentration are presented in Table 4.4.

Table 4.4 Effect of adsorption time on chromium and zinc ions adsorption[1]

Metal ion	Adsorption time (hrs)	Adsorbed concentration (ppm)[2]			
		A	B	C	D
Cr^{3+}	1	9.583 (± 0.005)	8.972 (± 0.005)	8.542 (± 0.004)	9.539 (± 0.005)
	2	9.564 (± 0.008)	8.922 (± 0.005)	8.324 (± 0.006)	8.608 (± 0.005)
	6	9.551 (± 0.005)	8.771 (± 0.007)	8.093 (± 0.005)	7.589 (± 0.005)
	12	9.326 (± 0.006)	8.608 (± 0.006)	7.589 (± 0.005)	6.895 (± 0.005)
	24	7.344 (± 0.005)	7.825 (± 0.005)	7.516 (± 0.005)	6.848 (± 0.005)
Zn^{2+}	1	8.630 (± 0.003)	8.367 (± 0.005)	8.152 (± 0.011)	8.344 (± 0.005)
	2	8.830 (± 0.005)	8.296 (± 0.004)	8.212 (± 0.005)	8.384 (± 0.005)
	6	8.824 (± 0.005)	8.222 (± 0.008)	8.030 (± 0.005)	8.327 (± 0.005)
	12	8.543 (± 0.005)	8.162 (± 0.005)	7.839 (± 0.010)	8.230 (± 0.005)
	24	8.322 (± 0.008)	8.010 (± 0.005)	7.663 (± 0.005)	8.139 (± 0.006)

[1] Initial Cr^{3+} and Zn^{2+} concentrations are 9.696 and 9.080 ppm, respectively at pH 7.00. 3 replicate adsorptions are performed.

[2] The SD of each average adsorbed concentration is the number in parentheses.

The adsorption efficiency of the effect of adsorption time was calculated and presented in Table 4.5

Table 4.5 Effect of adsorption time on adsorption efficiency[1]

Metal ion	Adsorption time (hrs)	Adsorption efficiency (%)			
		A	B	C	D
Cr^{3+}	1	98.84	92.53	88.10	98.38
	2	98.64	92.01	85.85	88.78
	6	98.51	90.46	83.46	78.26
	12	98.18	88.78	78.26	71.11
	24	75.74	80.70	77.52	70.63

Table 4.5 Effect of adsorption time on adsorption efficiency [1] (continued)

Metal ion	Adsorption time (hrs)	Adsorption efficiency (%)			
		A	B	C	D
Zn^{2+}	1	89.00	86.29	84.07	86.06
	2	91.07	85.56	84.69	86.47
	6	91.01	84.79	82.81	85.88
	12	88.11	84.17	80.81	84.88
	24	85.83	82.61	74.03	83.94

Figures 4.4 and 4.5 show the comparison of adsorption efficiency of chromium and zinc, respectively, by using 4 natural zeolites in the effect of adsorption time.

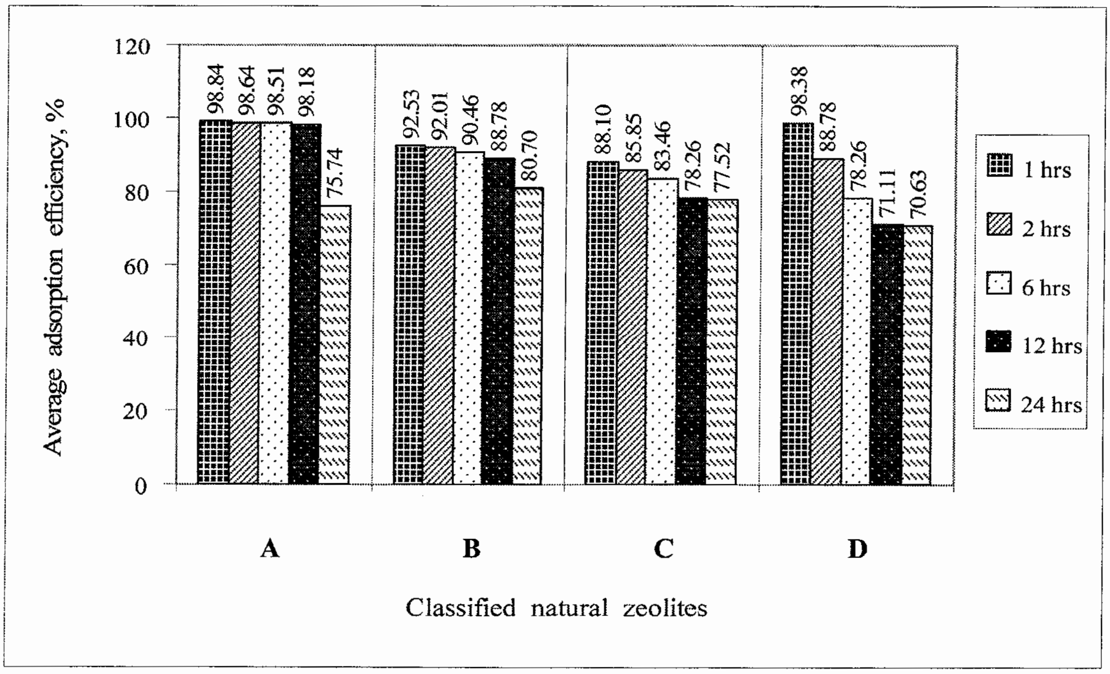

Figure 4.4 Comparison of adsorption efficiency of chromium by 4 natural zeolites on the effect of adsorption time

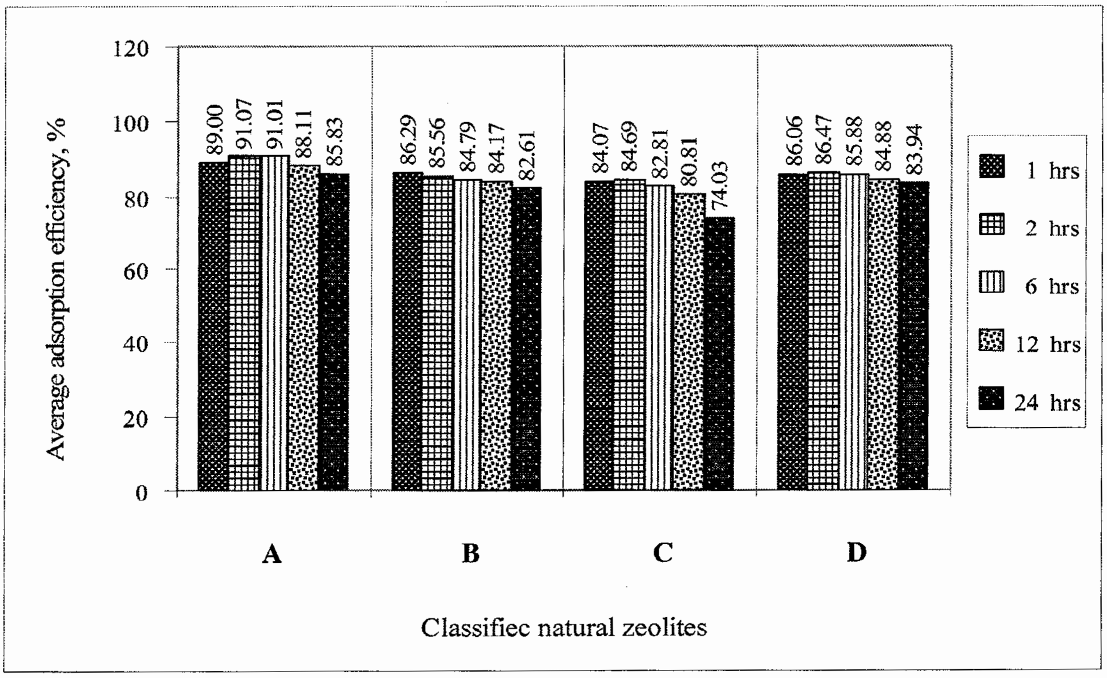

Figure 4.5 Comparison of adsorption efficiency of zinc by 4 natural zeolites on the effect of adsorption time

It is found that an hour is required to reach the maximum adsorption of metal ion on natural zeolites. Adsorption efficiency of metal from aqueous solution decreases with increasing the adsorption time. Desorption process may occur if metal ion adsorbed onto zeolite surface in longer time. Metal ion can be moved again into aqueous solution phase resulting in decreasing of metal ion removal efficiency from aqueous solution.

4.2.3 Effect of initial solution pH

Chromium and zinc ion were prepared in the form of aqueous solution by diluting of stock standard metal ion. The major ions in an aqueous are Cr^{3+} and Zn^{2+} in chromium and zinc solution, respectively. In addition, H^+ (proton or hydrogen ion) and OH^- (hydroxide ion) from water dissociation process in aqueous solution are major ionic species influencing for the adsorption of metal ions on natural zeolites. Effect of initial solution pH was investigated to ensure that the effect of H^+ or OH^- ions is competing to adsorb on zeolite surface. Presenting of H^+ in acidic solution, adsorption efficiency will be decreased because H^+ will compete the metal ions to adsorb on zeolite surface. Concerning adsorption of metal ions on natural zeolite surface in alkali solution, the result is similar to that of acidic solution. Because of presentation of OH^- in solution, precipitation of metal hydroxide compound will occur. Then metal species still present in solution. The removal efficiency of heavy metal ion will decrease (Oren and Kaya., 2006).

To investigate the effect of initial solution pH on adsorption of chromium and zinc, varying of initial solution pH at 3.0, 5.0, 7.0, 9.0 and 11.0 was performed by adjusting the initial solution pH with 0.10 M HCl or 0.10 M NaOH solution. The results of adsorbed metal ion concentration on the effect of initial solution pH are presented in Tables 4.6.

Table 4.6 Effect of initial solution pH on chromium and zinc ions adsorption[1]

Metal ion	pH	Adsorbed concentration (ppm)[2]			
		A	B	C	D
Cr^{3+}	3.0	8.005 (± 0.007)	8.232 (± 0.004)	7.962 (± 0.005)	7.782 (± 0.006)
	5.0	9.167 (± 0.005)	9.321 (± 0.005)	8.473 (± 0.006)	9.398 (± 0.005)
	7.0	10.231 (± 0.004)	9.559 (± 0.005)	9.300 (± 0.008)	9.979 (± 0.005)
	9.0	6.029 (± 0.005)	5.534 (± 0.005)	5.568 (± 0.005)	6.003 (± 0.007)
	11.0	3.745 (± 0.004)	3.117 (± 0.005)	2.307 (± 0.005)	3.374 (± 0.005)
Zn^{2+}	3.0	6.192 (± 0.005)	4.378 (± 0.008)	9.243 (± 0.005)	4.989 (± 0.005)
	5.0	7.500 (± 0.005)	5.221 (± 0.005)	3.779 (± 0.005)	5.919 (± 0.013)
	7.0	8.979 (± 0.004)	5.985 (± 0.007)	5.027 (± 0.005)	6.232 (± 0.008)
	9.0	5.783 (± 0.005)	3.723 (± 0.005)	3.018 (± 0.004)	4.506 (± 0.005)
	11.0	3.923 (± 0.005)	2.303 (± 0.006)	1.774 (± 0.005)	3.136 (± 0.008)

[1] Initial Cr^{3+} and Zn^{2+} concentrations are 10.452 and 10.262 ppm, respectively. 3 replicate adsorptions are performed.

[2] The SD of each average adsorbed concentration is the number in parentheses.

The adsorption efficiency of the effect of initial solution pH was calculated and presented in Table 4.7. It is found that

Table 4.7 Effect of initial solution pH on adsorption efficiency[1]

Metal ion	Metal ion concentration (ppm)	Adsorption efficiency (%)			
		A	B	C	D
Cr^{3+}	5.0 (5.037)	88.68	84.66	75.56	78.48
	10.0 (10.013)	80.45	72.62	67.34	69.09
	20.0 (20.076)	67.26	54.46	27.17	41.93
	30.0 (30.065)	55.60	41.39	15.81	21.69
Zn^{2+}	5.0 (5.017)	90.50	84.15	62.73	85.08
	10.0 (9.983)	82.62	74.36	54.72	78.76
	20.0 (20.055)	61.56	47.49	28.92	58.73
	30.0 (30.037)	48.46	27.11	10.39	43.87

The relationship between adsorption efficiency and initial solution pH for chromium and zinc removal is showed in Figures 4.6 and 4.7, respectively.

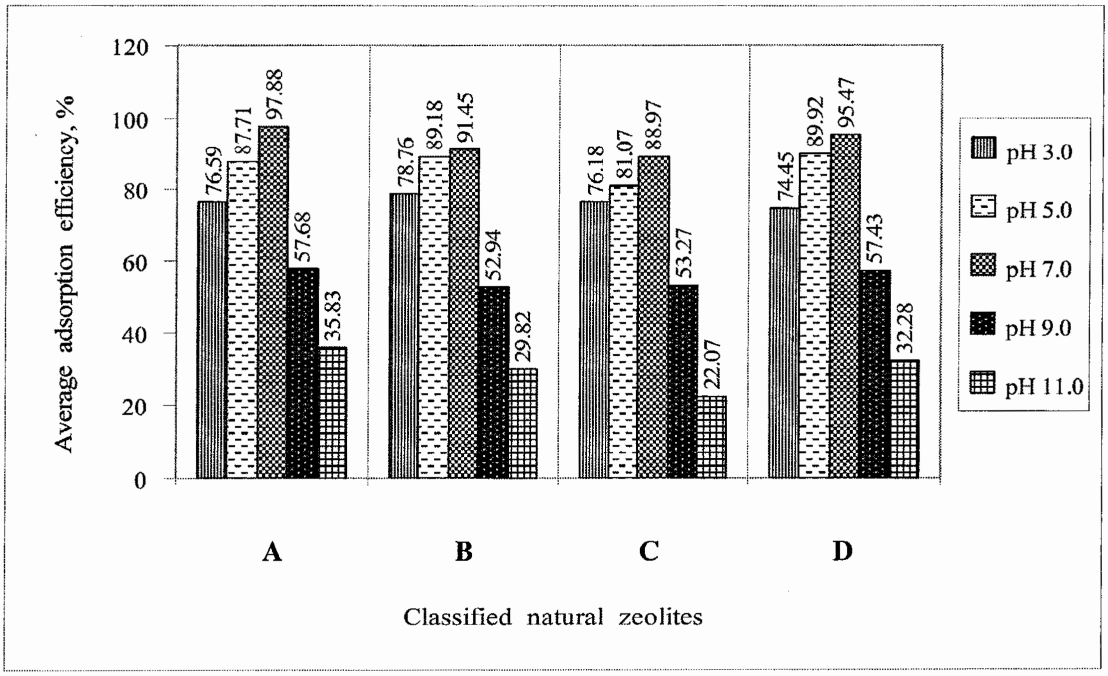

Figure 4.6 Comparison of adsorption efficiency of chromium by 4 natural zeolites on the effect of initial solution pH

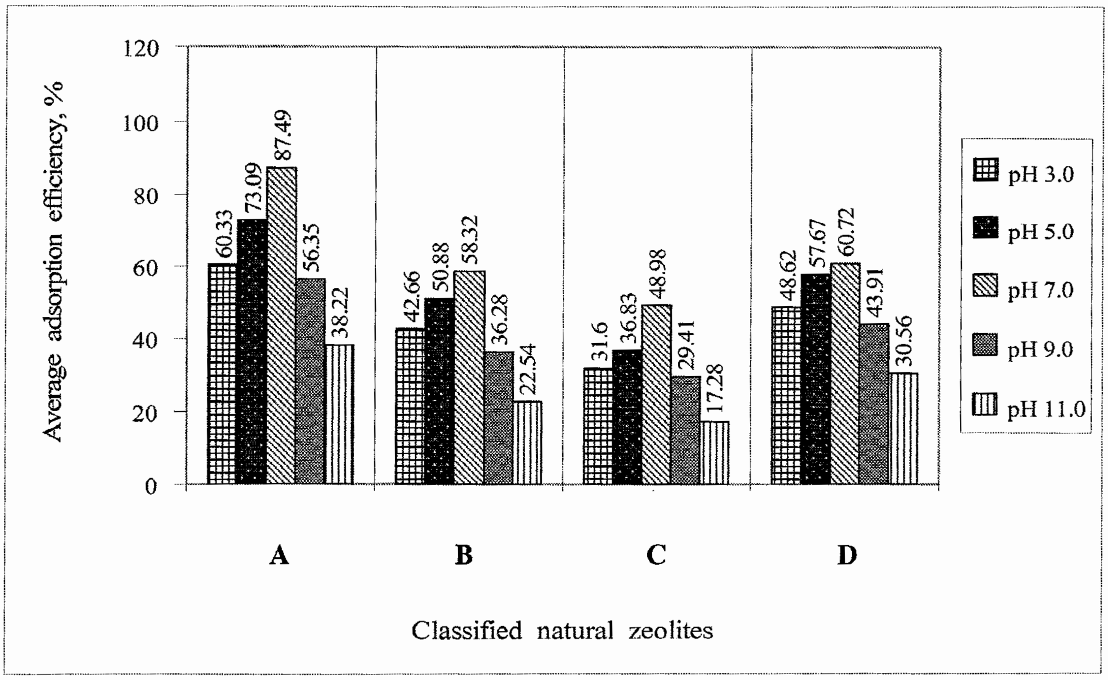

Figure 4.7 Comparison of adsorption efficiency of zinc by 4 natural zeolites on the effect of initial solution pH

Figures 4.6 and 4.7 show the change in adsorption efficiency of chromium and zinc, respectively. Adsorption efficiency increases when the initial solution pH is increased from 3.0 to 7.0. Decreasing in adsorption efficiency is occurred from pH 7.0 to 11.0. It is observed that removal efficiency is highest when batch adsorption was performed at pH 7.0.

In acidic solution, natural zeolites still have negative surface charge. It is the great advantage for the competition of H^+ to adsorb on zeolite surface. However, in basic solution, the formation of metal species with OH^- plays an important role in the decrease of metal ions removal above pH 7.0. With the condition of the higher pH solution (pH > 7), metal ion may forms complex ion with OH^- for example $Cr(OH)^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3$, $Cr(OH)_6^{3-}$ (Bosco and Enzweiler., 2002) and $Zn(OH)^+$, $Zn(OH)_2$, $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ (Peric, Trgo and Medvidovi., 2004). As a result, metal hydroxide species may precipitate into metal aqueous solution during the adsorption process.

4.2.4 Effect of initial metal ion concentration

To obtain the completely optimum condition for heavy metal adsorption, effect of initial metal ion concentration on adsorption of chromium and zinc was studied by varying on chromium and zinc working solution in the concentrations of 5.00, 10.00, 20.00 and 30.00 ppm. The results of adsorbed metal ion concentration are presented in Tables 4.8.

Table 4.8 Effect of initial metal ion concentration on adsorption efficiency[1]

Metal ion	Metal ion concentration (ppm)	Adsorbed concentration (ppm)[2]			
		A	B	C	D
Cr^{3+}	5.0 (5.037)	4.467 (± 0.005)	4.265 (± 0.004)	3.806 (± 0.007)	3.953 (± 0.005)
	10.0 (10.013)	8.055 (± 0.004)	7.272 (± 0.007)	6.743 (± 0.005)	6.918 (± 0.005)
	20.0 (20.076)	13.504 (± 0.005)	10.933 (± 0.005)	5.457 (± 0.004)	8.419 (± 0.004)
	30.0 (30.065)	16.717 (± 0.006)	12.445 (± 0.003)	4.753 (± 0.004)	6.520 (± 0.007)
Zn^{2+}	5.0 (5.017)	4.541 (± 0.005)	4.222 (± 0.007)	3.147 (± 0.005)	4.269 (± 0.008)
	10.0 (9.983)	8.248 (± 0.005)	7.423 (± 0.005)	5.463 (± 0.006)	7.863 (± 0.004)
	20.0 (20.055)	12.345 (± 0.005)	8.115 (± 0.004)	5.185 (± 0.004)	11.780 (± 0.007)
	30.0 (30.037)	14.557 (± 0.007)	8.142 (± 0.003)	3.122 (± 0.005)	13.177 (± 0.005)

[1] Initial Cr^{3+} and Zn^{2+} concentration (ppm) is the number in parentheses at pH 7.00. 3 replicate adsorptions are performed.

[2] The SD of each average adsorbed concentration is the number in parentheses.

The adsorption efficiency of the effect of initial metal ion concentration was calculated and presented in Table 4.9.

Table 4.9 Effect of initial metal ion concentration on chromium and zinc ions adsorption[1]

Metal ion	Metal ion concentration (ppm)	Adsorption efficiency (%)			
		A	B	C	D
Cr^{3+}	5.0 (5.037)	88.68	84.66	75.56	78.48
	10.0 (10.013)	80.45	72.62	67.34	69.09
	20.0 (20.076)	67.26	54.46	27.17	41.93
	30.0 (30.065)	55.60	41.39	15.81	21.69

Table 4.9 Effect of initial metal ion concentration on chromium and zinc ions adsorption[1] (continued)

Metal ion	Metal ion concentration (ppm)	Adsorption efficiency (%)			
		A	B	C	D
Zn^{2+}	5.0 (5.017)	90.50	84.15	62.73	85.08
	10.0 (9.983)	82.62	74.36	54.72	78.76
	20.0 (20.055)	61.56	47.49	28.92	58.73
	30.0 (30.037)	48.46	27.11	10.39	43.87

The relationship between adsorption efficiency and initial metal ion concentration for chromium and zinc removal is also showed in Figures 4.8 and 4.9, respectively.

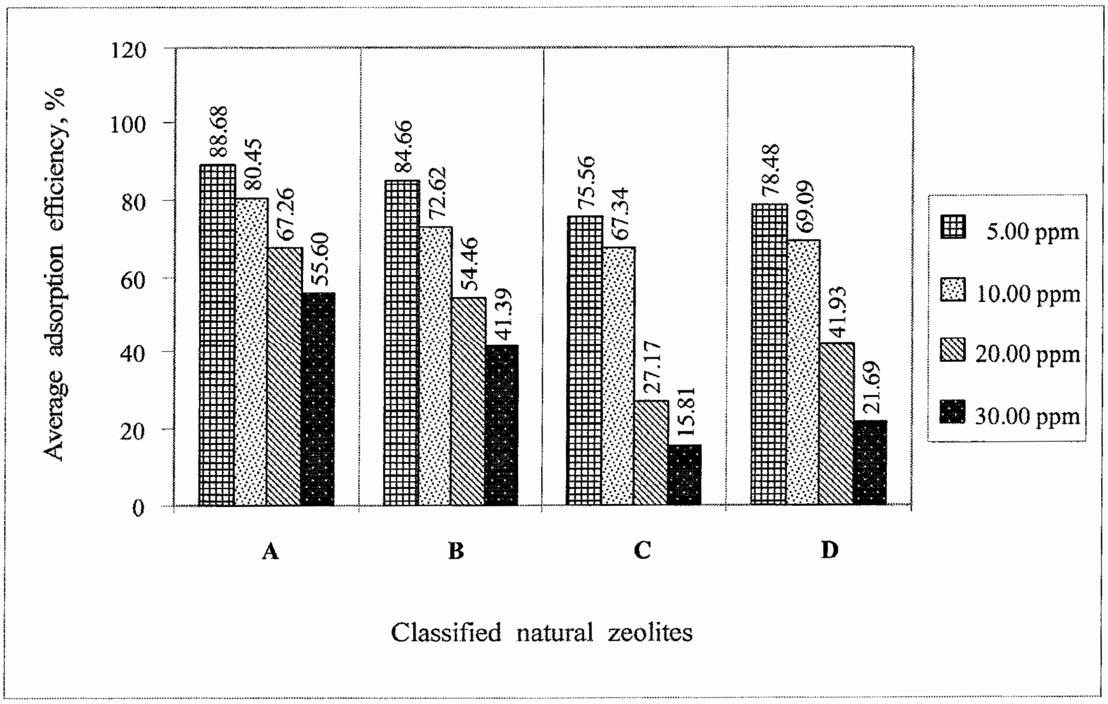

Figure 4.8 Comparison of adsorption efficiency of chromium by 4 natural zeolites on the effect of initial metal ion concentration

From Figure 4.8, the result of maximum adsorption efficiency was obtained at the concentration of 5.00 ppm initial chromium working solution. Adsorption efficiencies of chromium by natural zeolites A, B, C and D are 88.68%, 84.66%, 75.56% and 78.48%, respectively. It is observed that adsorption efficiency of chromium decreases at the higher initial concentration (10.00, 20.00 and 30.00 ppm).

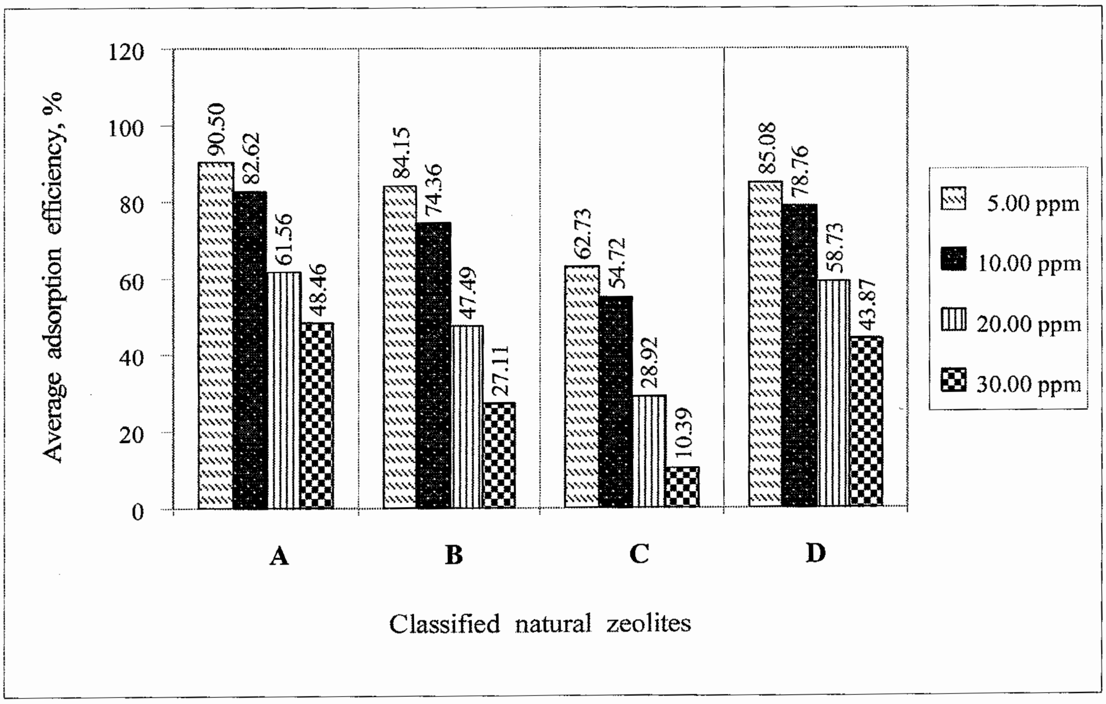

Figure 4.9 Comparison of adsorption efficiency of zinc by 4 natural zeolites on the effect of initial metal ion concentration

Figure 4.9, the trend of zinc adsorption efficiency is similar to chromium adsorption efficiency. The result of maximum adsorption efficiency was obtained at the concentration of 5.00 ppm initial zinc working solution. Maximum adsorption efficiencies of zinc by natural zeolites A, B, C and D is 90.50%, 84.15%, 62.73% and 85.08%, respectively.

It is found that adsorption efficiencies of chromium and zinc decrease with increasing the concentration of metal ion in aqueous solutions. These results indicate that the numbers of active site for adsorption of metal ion are similar to in all metal ion concentration although batch adsorption was carried out on various metal ion concentration experiments. Metal ions are not adsorbed on zeolite surface but it is still retained in an aqueous solution.

4.3 INVESTIGATION OF ADSORPTION ISOTHERMS

The adsorption data of chromium and zinc using 4 natural zeolites as adsorbents have been subjected to 2 adsorption isotherms. Freundlich and Langmuir isotherms were selected to study the effect of initial metal ion concentration concerning adsorbed behavior onto natural zeolite. The obtained experimental data are expectedly well fitted with the linearized form of 2 mathematic models.

4.3.1 Freundlich isotherm

The Freundlich adsorption isotherm is one of the most widely used mathematical descriptions. It is usually fitting the experimental data over a wide range of concentrations. This isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies.

The Freundlich adsorption isotherm is applied to the removal of chromium and zinc ions on zeolite surface as the equation following;

$$\log C_{ads} = 1/n \log C_e + \log K$$

Where;	C_e	is	the equilibrium concentration of metal ions in solution
	C_{ads}	is	the concentration of metal ions adsorbed onto zeolite
	K	is	a parameter related to the temperature
	n	is	a characteristic constant for the adsorption system under study

K and n were calculated for each metal ion. A value of n between 2 to 10 shows good adsorption. The numerical value of $1/n < 1$ indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations. This isotherm does not predict any saturation of the adsorbent by the adsorbate on infinite surface coverage. It is predicted mathematically and indicating a multilayer adsorption on the surface.

A linear plot was obtained when log C_e is plotted against log C_{ads} over the entire concentration range of chromium ions investigated. The Freundlich adsorption isotherms for adsorption of chromium ions on natural zeolites A, B, C and D are plotted in Figure 4.6.

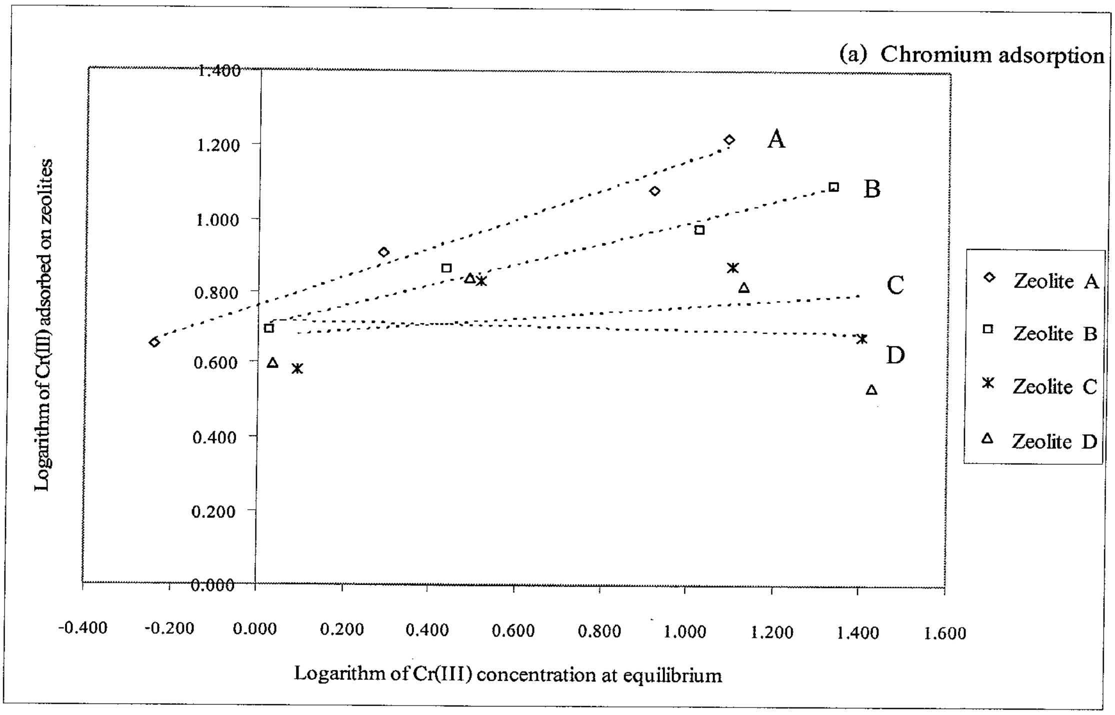

Figure 4.10 Freundlich adsorption isotherms of chromium ions on natural zeolite A, B, C and D

As shown from Figure 4.10, the experimental data, K, 1/n and n was obtained from Freundlich model and presented in Table 4.10. It is observed that adsorption isotherm of zeolite A and B well fit with the linearized Freundlich isotherm with determination coefficient values (R^2) of 0.9766 and 0.9771, respectively. However, the isotherms for zeolites C and D are not reliability because R^2 values are very low. The value of n between 2-10 shows good adsorption but it is over ranking with zeolites C and D. There are 11.5607 and -43.4783, respectively, showing the bad adsorption of chromium ions on natural zeolites C and D.

Table 4.10 Experimental data and Freundlich parameters of chromium adsorption

Classified natural zeolites	Concentration of Cr^{3+} solution (ppm)[1]	Freundlich parameters					
		log C_e	log C_{ads}	K	1/n	n	R^2
A	5.00 (5.037)	-0.240	0.650	5.7584	0.3976	2.5151	0.9766
	10.00 (10.013)	0.290	0.910				
	20.00 (20.076)	0.920	1.080				
	30.00 (30.065)	1.090	1.220				
B	5.00 (5.037)	0.026	0.693	5.0431	0.2882	3.4698	0.9771
	10.00 (10.013)	0.438	0.862				
	20.00 (20.076)	1.027	0.975				
	30.00 (30.065)	1.335	1.095				
C	5.00 (5.037)	0.090	0.581	4.7044	0.0863	11.5607	0.1410
	10.00 (10.013)	0.515	0.829				
	20.00 (20.076)	1.101	0.873				
	30.00 (30.065)	1.403	0.677				
D	5.00 (5.037)	0.035	0.597	5.2024	-0.0230	-43.4783	0.0087
	10.00 (10.013)	0.491	0.840				
	20.00 (20.076)	1.129	0.820				
	30.00 (30.065)	1.425	0.537				

[1] Initial Cr^{3+} concentration (ppm) is the number in parentheses at pH 7.00

There are also plotted a linear of log C_e against log C_{ads} over the entire concentration range of zinc ions investigated. The Freundlich adsorption isotherms for adsorption of zinc ions on natural zeolites A, B, C and D are plotted in Figure 4.11.

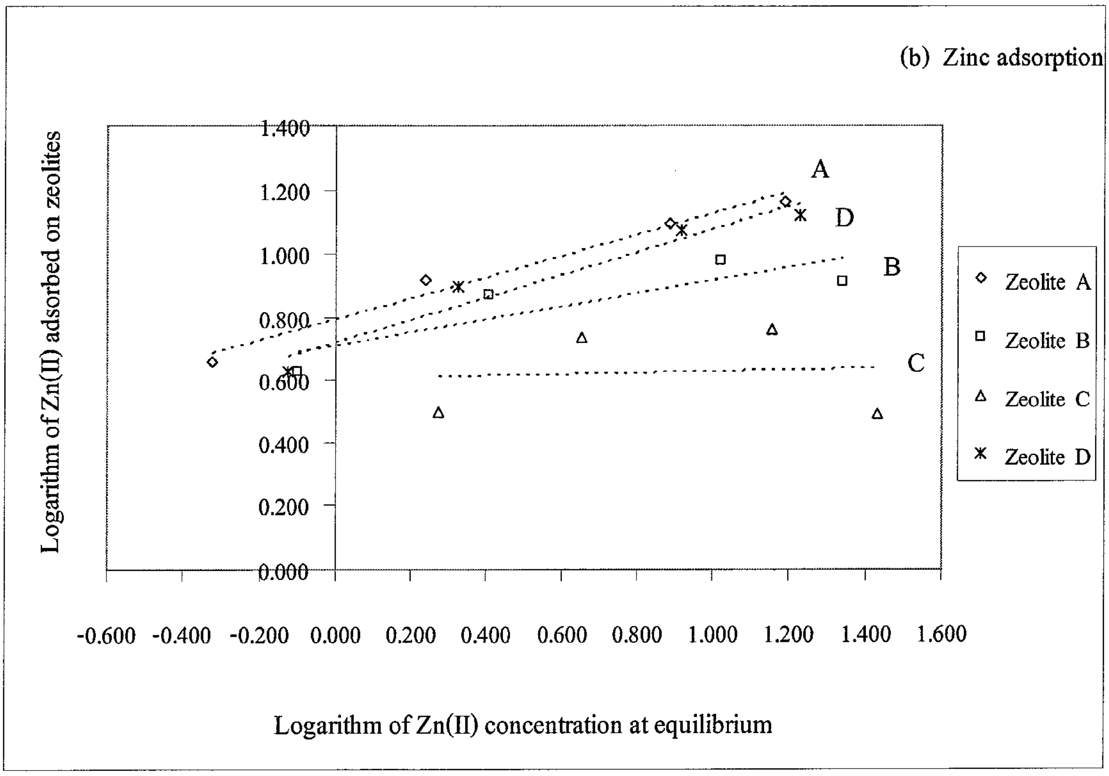

Figure 4.11 Freundlich adsorption isotherms of zinc ions on natural zeolite A, B, C and D

As shown from Figure 4.11, K, 1/n and n were obtained from Freundlich model and presented in Table 4.11. It is observed that adsorption isotherm of zeolite A and D well fit with the linearized Freundlich isotherm with R^2 values as 0.9777 and 0.9489, respectively. Zeolite B and C are not reliability because R^2 value of B is low (0.7325) while R^2 value of C is the lowest (0.0063). The n value between 2-10 shows good adsorption. The n value of zeolite C is over ranking (44.0529) that shows the bad adsorption of zinc ions occurred on natural zeolite C.

Table 4.11 Experimental data and Freundlich parameters of zinc adsorption

Classified natural zeolites	Concentration of Zn^{2+} solution (ppm)[1]	Freundlich parameters					
		log C_e	log C_{ads}	K	1/n	n	R^2
A	5.00 (5.017)	-0.322	0.657	6.2044	0.3296	3.034	0.9778
	10.00 (9.983)	0.239	0.916				
	20.00 (20.055)	0.887	1.092				
	30.00 (30.037)	1.190	1.163				
B	5.00 (5.017)	-0.099	0.626	5.1204	0.2053	4.8709	0.7325
	10.00 (9.983)	0.408	0.871				
	20.00 (20.055)	1.022	0.979				
	30.00 (30.037)	1.340	0.911				
C	5.00 (5.017)	0.272	0.498	4.0124	0.0227	44.0529	0.0063
	10.00 (9.983)	0.655	0.737				
	20.00 (20.055)	1.154	0.763				
	30.00 (30.037)	1.430	0.494				
D	5.00 (5.017)	-0.126	0.630	5.2481	0.3569	2.8019	0.9489
	10.00 (9.983)	0.326	0.896				
	20.00 (20.055)	0.918	1.071				
	30.00 (30.037)	1.227	1.120				

[1] Initial Zn^{2+} concentration (ppm) is the number in parentheses at pH 7.00

It is observed that Freundlich isotherms of chromium and zinc adsorption on natural zeolite are not consistent to the results from all previous investigated. Moreover, there are not corresponding to the selectivity and adsorption capacity as the sequence following; for chromium ion adsorption, zeolite A > zeolite B > zeolite D > zeolite C and for zinc ion adsorption; zeolite A > zeolite D > zeolite B > zeolite C.

4.3.2 Langmuir isotherm

The equilibrium data for metal ions over the concentration range from 5.00 to 30.00 ppm at room temperature have been correlated with the Langmuir isotherms;

$$C_e/C_{ads} = C_e/Q + 1/Qb$$

Where; C_e is the equilibrium concentration of metal ions in solution
C_{ads} is the concentration of metal ions adsorbed onto zeolite
Q is Langmuir constants related to sorption capacity
b is Langmuir constants related to sorption energy

Maximum sorption capacity (Q) represents monolayer coverage of metal ion (as adsorbate) with natural zeolite (as adsorbent) and b represents enthalpy of sorption which varies with temperature. Minimum value of b represents chemical bonding between metal ion and zeolites are strong and stable. A linear plot is obtained when C_e is plotted against C_e/C_{ads} over the entire concentration range of metal ions investigated.

Langmuir isotherm was also studied. A linear plot of C_e/C_{ads} was plotted against C_e over the entire concentration range of chromium ions investigated. The Langmuir adsorption isotherms for adsorption of chromium ions on natural zeolites A, B, C and D are plotted in Figure 4.12.

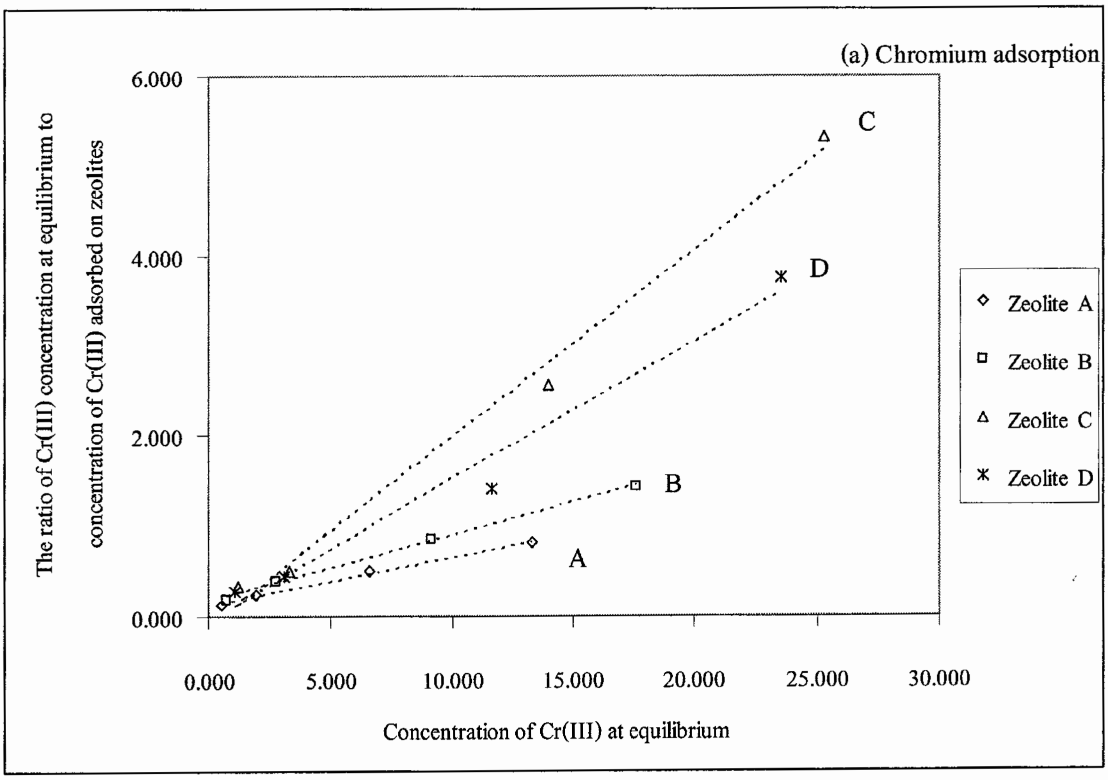

Figure 4.12 Langmuir adsorption isotherms of chromium ions on natural zeolite A, B, C and D

The Langmuir parameters and the statistical fits of the adsorption data are presented in Table 4.12. The Langmuir model effectively describes the adsorption data with all R^2 values >0.9750. According to the Q value parameter, the sequence of chromium ion adsorption on natural zeolites is presented as following; zeolite A (19.4553) > zeolite B (13.8504) > zeolite D (6.4350) > zeolite C (4.7664). The obtained results are consistent to the results of chromium ion adsorption on natural zeolite from the preliminary adsorption study.

Table 4.12 Experimental data and Langmuir parameter for chromium adsorption

Classified natural zeolites	Concentration of Cr^{3+} solution (ppm)[1]	Langmuir parameters					
		C_e	C_{ads}	C_e/C_{ads}	Q	b	R^2
A	5.00 (5.037)	0.570	4.467	0.128	19.4553	0.4089	0.9934
	10.00 (10.013)	1.958	8.055	0.243			
	20.00 (20.076)	6.572	13.504	0.487			
	30.00 (30.065)	13.348	16.717	0.799			
B	5.00 (5.037)	0.773	4.265	0.181	13.8504	0.4631	0.9978
	10.00 (10.013)	2.742	7.272	0.377			
	20.00 (20.076)	9.144	10.933	0.836			
	30.00 (30.065)	17.620	12.445	1.416			
C	5.00 (5.037)	1.231	3.806	0.323	4.7664	-1.6920	0.9923
	10.00 (10.013)	3.270	6.743	0.485			
	20.00 (20.076)	13.980	5.470	2.556			
	30.00 (30.065)	25.310	4.753	5.325			
D	5.00 (5.037)	1.084	3.953	0.274	6.4350	-2.5105	0.9754
	10.00 (10.013)	3.096	6.918	0.448			
	20.00 (20.076)	11.658	8.419	1.385			
	30.00 (30.065)	23.545	6.250	3.767			

[1] Initial Cr^{3+} concentration (ppm) is the number in parentheses at pH 7.00

A linear plot of zinc ions adsorption on 4 natural zeolites is also obtained when C_e is plotted against C_e/C_{ads} over the entire concentration range of zinc ions investigated. The Langmuir adsorption isotherms for adsorption of zinc ions on natural zeolites A, B, C and D are plotted in Figure 4.13.

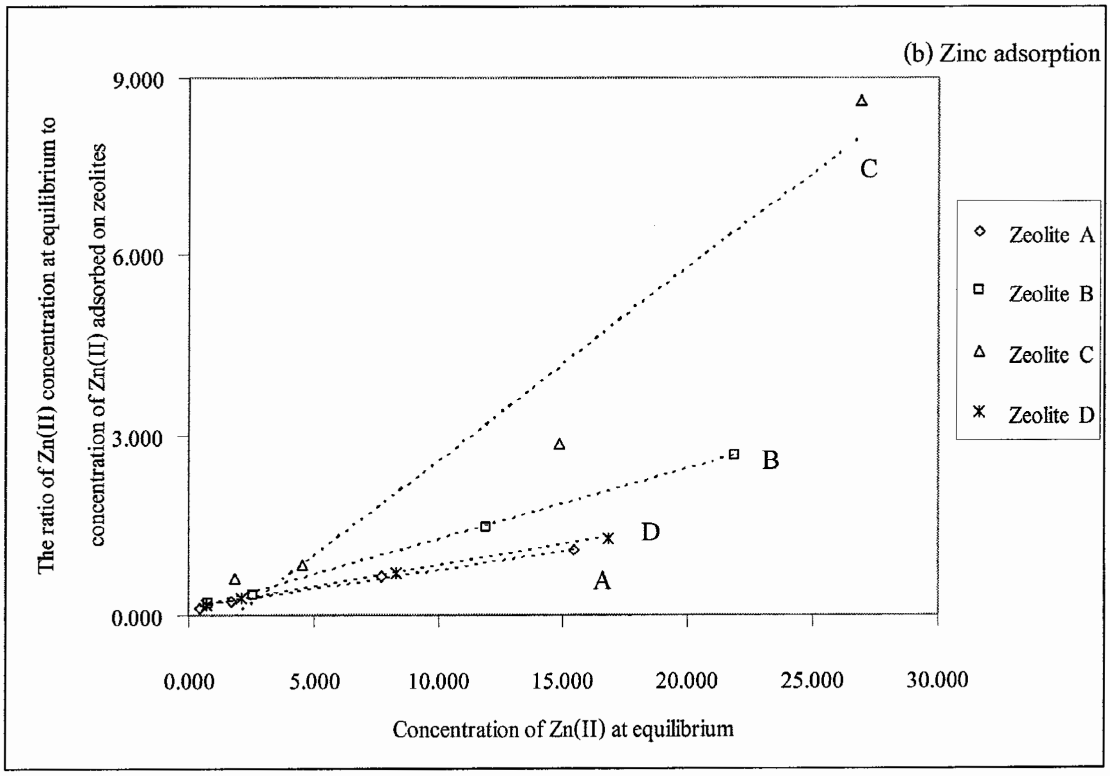

Figure 4.13 Langmuir adsorption isotherms of zinc ions on natural zeolite A, B, C and D

The Langmuir parameters and the statistical fits of the adsorption data of zinc ion adsorbed on 4 natural zeolites are given in Table 4.13. The Langmuir model effectively describes the adsorption data with all R^2 values >0.9950 excepted isotherm of zeolite C given R^2 value at 0.9431 that it still acceptable. According to the Q value parameter, zinc ion adsorption on natural zeolites is produced following the sequence A (15.7233) > zeolite D (14.5773) > zeolite B (8.3752) > zeolite C (3.1378) that consistent to the results of zinc ions adsorption on natural zeolite from part 4.2, preliminary metal adsorption study.

Table 4.13 Experimental data and Langmuir parameter for zinc adsorption

Classified natural zeolites	Concentration of Zn^{2+} solution (ppm)[1]	Langmuir parameters					
		C_e	C_{ads}	C_e/C_{ads}	Q	b	R^2
A	5.00 (5.017)	0.477	4.541	0.105	15.7233	0.6570	0.9961
	10.00 (9.983)	1.735	8.248	0.210			
	20.00 (20.055)	7.710	12.345	0.625			
	30.00 (30.037)	15.480	14.557	1.063			
B	5.00 (5.017)	0.795	4.222	0.188	8.3752	1.8922	0.9995
	10.00 (9.983)	2.560	7.423	0.345			
	20.00 (20.055)	11.940	8.115	1.471			
	30.00 (30.037)	21.895	8.142	2.689			
C	5.00 (5.017)	1.870	3.147	0.594	3.1378	-0.5221	0.9431
	10.00 (9.983)	4.520	5.463	0.827			
	20.00 (20.055)	14.870	5.185	2.868			
	30.00 (30.037)	26.920	3.122	8.623			
D	5.00 (5.017)	0.749	4.269	0.175	14.5773	0.5427	0.9999
	10.00 (9.983)	2.120	7.863	0.270			
	20.00 (20.055)	8.275	11.780	0.703			
	30.00 (30.037)	16.860	13.177	1.280			

[1] Initial Zn^{2+} concentration (ppm) is the number in parentheses at pH 7.00

Based on the adsorption isotherm studies, determination coefficient (R^2) presented in Tables 4.10, 4.11, 4.12 and 4.13. It is indicated that the adsorption data for chromium and zinc adsorption fitted well the Langmuir isotherm for all classified natural zeolites. The Langmuir model parameters and the statistical fits of the adsorption data to this equation are also presented in Tables 4.12 and 4.13. The Langmuir model effectively described the sorption data with all R^2 values > 0.9750. Only the adsorption of zinc by classified natural zeolite C is excepted because the R^2 is 0.9431. According to the Q parameter, adsorption of chromium is producing following the sequence: zeolite A (19.4553) > zeolite B (13.8504) > zeolite D (6.4350) > zeolite C (4.7664) and adsorption of zinc is producing following the sequence: zeolite A (15.7233) > zeolite D (14.5773) > zeolite B (8.3752) > zeolite C (3.1378). It is observed that 2 sequences are the same and consistent to the results the preliminary of both metals adsorption studied.

CHAPTER 5

CONCLUSSIONS AND RECOMMENDATION

5.1 CONCLUSION

The Thai natural zeolites found in the region of Songkhla province, the south of Thailand, have proved its adsorption property in chromium and zinc removal from prepared aqueous solution on a laboratory scale by batch adsorption experiment. The following conclusions can be drawn from the results of the experiments in this study:

5.1.1 Preliminary adsorption study of chromium ions by natural zeolites was performed by suspended 40 g/l of each natural zeolite in 10.00 ppm of chromium ion solution for an hour. The adsorption efficiency of classified natural zeolites was sequenced as A > B > D > C > E > F > G giving adsorption efficiency of 95.06%, 92.73%, 92.49%, 88.90%, 68.67%, 62.21% and 51.31%, respectively. While, the adsorption efficiency of zinc ions was obtained on the same condition as chromium adsorption. The adsorption efficiency was sequenced from A > D > B > C > E > F > G giving adsorption efficiency of 82.38%, 60.75%, 57.84%, 48.19%, 16.90%, 16.77% and 16.61%, respectively.

5.1.2 The optimum condition for chromium adsorption was obtained by suspended each 20.0 g/l of zeolite A and 30.0 g/l of zeolites B, C and D in 5.00 ppm chromium solution at pH 7.0 for an hour adsorption time. Systematic perturbation was performed at the time of 30 minutes for 30 seconds while, the optimum condition for zinc adsorption was obtained by suspended each 30.0 g/l of zeolites A, B, C and D in 5.00 ppm zinc solution at pH 7.0 for an hour adsorption time. Systematic perturbation was performed at the time of 30 minutes for 30 seconds.

5.1.3 The experiment results of chromium and zinc were well fit with the Langmuir isotherms because of the results of Langmuir isotherm for both metals were corresponded to the results of preliminary adsorption study. In addition, Langmuir isotherms have a better correspondence with the experimental findings rather than with Freundlich isotherm because of all R^2 values of Langmuir isotherm model >0.95.

5.2 RECOMMENDATION FOR FUTURE WORK

This obtained optimum conditions for adsorption of chromium and zinc by Thai natural zeolite from Songkhla province should be applied in treatment of real wastewater sample.

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APPENDIX

POSTER CONTRIBUTIONS TO CONFERENCES

1. INTERNATIONAL CONFERENCE

Atit Jirochphakorn, Saisamorn Lumlong, Duangdao Sattayakul, Matana Kacha, Nithiporn Luckhasorn, Waraporn Sisan, Rungnapa Tipakontitikul, Anuson Niyompan, Anchana Sangthong, Usa Onthong and Pornpan Pungpo. Structural characterization of Thai natural zeolites by using XRD and XRF techniques and their environmental applications for zinc removal from aqueous solution: laboratory scale. *Pure and Applied Chemistry International Conference 2008, January, 3-February, 1, 2008, Bangkok, Thailand.*

2. NATIONAL CONFERENCE

Atit Jirochphakorn, Saisamorn Lumlong, Duangdao Sattayakul, Matana Kacha, Nithiporn Luckhasorn, Waraporn Sisan, Rungnapa Tipakontitikul, Anuson Niyompan, Usa Onthong and Pornpan Pungpo. Structural characterization of natural zeolites by using x-ray diffraction and x-ray fluorescence spectroscopy techniques and its environmental applications for removal of Zinc ion from aqueous solution. *The 33rd Congress on Science and Technology of Thailand, October, 18-20, 2007, Nakhon Si Thammarat, Thailand.*

Structural Characterization of Thai Natural Zeolites by using XRD and XRF Techniques and Their Environmental Applications for Zinc Removal from Aqueous Solution: Laboratory Scale

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ABSTRACT

Three natural zeolites found in Songkhla province, Thailand, have been characterized using XRD and XRF spectroscopy techniques. The obtained XRD patterns were compared with the patterns given in the ICDB number. The results reveal that the profiles correspond to modernite ($(Na_2,Ca,K_2)Al_2Si_{10}O_{24}.7H_2O$), clinoptiolite ($(Na,K,Ca)_5Al_6Si_{30}O_{72}.18H_2O$) and kaolinite-1MD ($Al_2Si_2O_5(OH)_4$) for natural zeolites no.1, no.2 and no.3, respectively. For XFR results, it was found that the information obtained XRF analysis could support the structural data derived by the XRD pattern. Then, all zeolites have been applied to remove zinc ions from aqueous solution at laboratory scale. The result show that thai natural zeolites of kaolinite-1MD, mordenite and clinoptiolite are successfully used to reduce Zn^{2+} from solution with adsorption efficiency of 90.50%, 89.0% and 86.06% respectively. The optimum conditions for adsorption efficiency are listed as following: the initial concentration of 10 mg/L with pH at 7, an hour adsorption time and 40 g/L of the zeolite usage per Zn^{2+} solution volume. Base on the adsorption isotherm studies, the obtained isotherm is in consistent to the Langmuir isotherms. This obtained result indicates that, at laboratory scale, kaolinite-1MD serves as a highly effective adsorbent, whereas mordenite and clinoptiolite show comparable adsorption capacities for zinc ion in aqueous solution. Accordingly, these findings show that the natural zeolites are recommendable natural adsorbents for highly zinc ion removal in large scale unit for wastewater treatment with low-cost treatment and environmentally friendly chemical processes.

Keywords
Heavy metal removal, natural zeolites, adsorption

1. INTRODUCTION

Zeolites are naturally occurring hydrated aluminosilicate minerals. They have a three-dimensional structure constituted by $(Si, Al)O_4$ tetrahedra connected by all their oxygen vertices forming channels where H_2O molecules and exchangeable cations counterbalancing the negative charge generated from the isomorphous substitution are present. Zeolites have many applications, mainly based on their structural characteristics, their sorbent properties and their relatively high specific surface area. Nowadays, the increasing levels of heavy metals in the environment represent a serious threat to human health, living resources and ecological systems. Zeolites minerals have been proposed as sorbent phases in the treatment of drinkable water or industrial wastewater containing toxic metal species [1-5]. The main objectives of the present work are to characterize thai natural zeolites and to study the applicability of thai natural zeolites on the removal of zinc ion from aqueous solution.

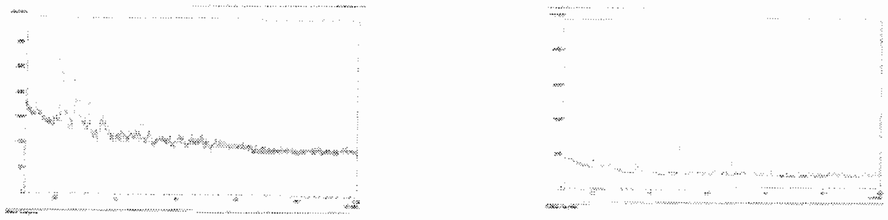
2. METHODS OF CALCULATIONS

Three natural zeolites found in the Songkhla province were applied for zinc ion treatment from aqueous solution. For characterization of natural zeolites, the X-ray diffraction (XRD) patterns were acquired on a Philips X'Pert MPD, using CuK$_\alpha$ radiation source (λ=1.54 nm) at 45 kV and 35 mA. Each sample was measured in the range of $5° \le 2\theta \le 120°$ with scanning rate 0.04 2θ/sec at room temperature. The X-ray fluorescence (XRF) were performed on a Philips MagiX WDXRF. For water samples used in this study, the 10 ppm concentration of zinc solution was prepared by using Zn stock solution in de-ionized water. To measure the exact concentration of the metal ion before and after treatments by zeolite, atomic absorption spectroscopy (Perkin Elmer Model Analyst 800) was used.

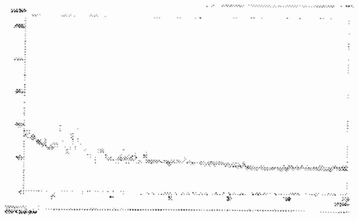
3. RESULTS AND DISCUSSION

3.1 Structural characterization of natural zeolites

In order to characterize the structure of three natural zeolites, XRD analysis was performed. The XRD pattern is shown in Figure 1. The obtained XRD patterns were compared with the patterns given in the ICDB number. The results reveal that the profiles correspond to Modernite ($(Na_2,Ca,K_2)Al_2Si_{10}O_{24}.7H_2O$), Clinoptiolite ($(Na,K,Ca)_5Al_6Si_{30}O_{72}.18H_2O$) and Kaolinite-1Md ($Al_2Si_2O_5(OH)_4$) compounds for natural zeolites no.1, no.2 and no.3, respectively. For XFR results, the elemental compositions of the zeolites were analyzed as reported in Table 1. It was found that the information obtained XRF analysis could support the structural data derived by the XRD pattern.



no.1 no.2



no.3

Figure 1. X-ray diffraction pattern of three natural zeolites, no.1-3.

3.2 Applications of natural zeolites in the removal of zinc ion from aqueous solution

As the metal removal efficiency was affected by adsorption time and ratio of zeolite usage per water sample volume, the optimal parameters for the adsorption have to be determined. Modernite was selected to use for the adsorption preliminary study. To study the effect of zeolite amount, modernite was weighted and varied from 1.00, 1.50, 2.00, 2.50 and 3.00 g. Then, all suspension were carried out in 50 mL of each 10 mg/L metal solution at pH 7. All batch adsorptions were performed for an hour. The removal efficiency of zinc ion from aqueous solutions is 49.67%, 59.16%, 67.62%, 75.58% and 79.97%, respectively. The result showed that 2.5 g of modernite was optimum amount for the zinc adsorption. To study the effect of contact time for adsorption, the natural zeolite was weighted as the optimum amount obtained from from the previous step. Then, all suspension were carried out in 50 mL of metal solution at pH 7. All batch adsorptions were varied from 1, 2, 6, 12 and 24 hours, respectively. The zinc ion removal efficiency of 89.00 %, 91.07 %, 91.01 %, 88.11 % and 85.83 % were derived, respectively. The optimum contact time for zinc adsorption is an hour. Therefore, an hour adsorption time and 50 g/L of the ratio of zeolite per water sample are chosen as optimal adsorption parameters for further step.

Consecutively, two natural zeolites, Clinoptiolite and Kaolinite-1MD were used as adsorbents for zinc ions removal from sample water based on adsorption parameters derived from the preliminary study. The results show that zinc ions were removed from aqueous solution with average removal efficiency of 86.06 %, and 90.50 %, respectively. The order of removal efficiency of zinc ions removal of three natural zeolites can be listed as Kaolinite-1MD ≈ Mordenite > Clinoptiolite.

Table 1. The element compositions of three natural zeolites, derived by XRF spectroscopy.

Elements	**Concentration (%)**		
	No.1	**No.2**	**No.3**
O	49.47	50.80	50.32
Si	33.52	31.34	24.36
Al	6.726	15.18	4.829
Ca	4.405	0.1478	7.857
K	2.451	0.4484	1.861
Fe	1.394	0.7995	0.8847
S	1.003	0.06787	9.140
P	0.4226	0.4590	0.3131
Mg	0.3719	<<	0.3153
Ti	0.1810	0.5987	0.1172
Mn	0.05526	-	<<
Au	0.0000	0.0000	0.0000
Zr	0.0000	0.0000	0.0000
Sr	0.0000	-	0.0000
Rb	0.0000	0.0000	-
Se	0.0000	0.0000	0.0000
Y	<<	-	-
Ce	-	-	-
Cl	-		-

3.3 Adsorption isotherm of zinc ion from aqueous solution on the natural zeolite

The sorption data of zinc by the natural zeolite have been subjected to two sorption isotherms, namely, Freundlich and Langmuir isotherms to study the effect of initial metal ion concentration for adsorption behavior onto natural zeolite. Kaolinite-1MD was used as the hightest effective adsorbent in this study. The results show that the Langmuir model effectively described the sorption data with high R^2 values (0.9999) compared with that obtained from Freundlich adsorption isotherm. It is clearly seen that Langmuir isotherms have a better correspondence with the experimental findings rater that Freundlich isotherm.

Figure 2 Freundlich adsorption isotherm for zinc ions on the natural zeolite Kaolinite-1MD

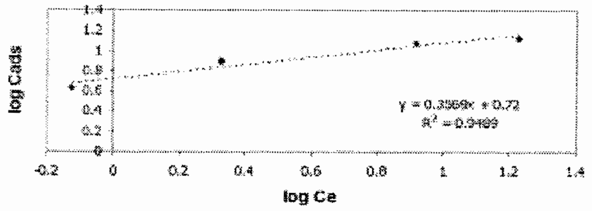
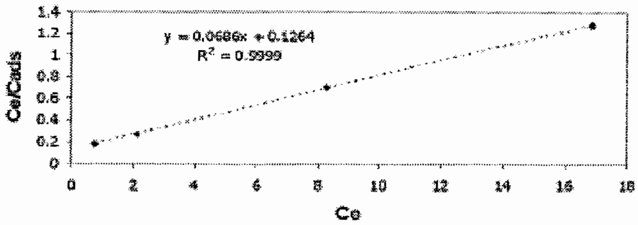


Figure 3. Langmuir adsorption isotherm for zinc ions on the natural zeolite Kaolinite-1MD



4. CONCLUSIONS

In summary, three thai natural zeolites have been characterized and environmentally applied as effective adsorbents. The natural zeolites used show high adsorption capacities for zinc ion from aqueous solution. These findings show that both kaolinite-1MD and mordenite can be used as highly potential adsorbent for the removal of zinc ions from wastewater. For adsorption isotherms, Langmuir isotherms have a better correspondence with the experimental findings rather than with Freundlich isotherm. Based on the present study, it can be seen that the natural zeolites are effectively used for removing zinc ion from aqueous solution. These findings are beneficial information for practical applications in industrial wastewater treatment with high efficiency and relatively low cost materials.

5. ACKNOWLEDGMENTS

Research supports from Division of Research Promotion, Ubonratchathani University and Faculty of Science, Ubonratchathani University are gratefully acknowledged.

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Structural Characterization of Thai Natural Zeolites by using XRD and XRF Techniques and Their Environmental Applications for Zinc Removal from Aqueous Solution: Laboratory Scale

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INTRODUCTION

Zeolites are naturally occurring hydrated aluminosilicate minerals. They have a three-dimensional structure constituted by $(Si,Al)O_4$ tetrahedra connected by all their oxygen vertices forming channels where H_2O molecules and exchangeable cations counterbalancing the negative charge generated from the isomorphous substitution are present. Zeolites have many applications, mainly based on their structural characteristics, their adsorbent properties and their relatively high specific surface area. Nowadays, the increasing levels of heavy metals in the environment represent a serious threat to human health, living resources and ecological systems. Zeolites minerals have been proposed as adsorbent phases in the treatment of drinkable water or industrial wastewater containing toxic metal species. The main objectives of the present work are to characterize Thai natural zeolites and to study the applicability of Thai natural zeolites on the removal of zinc ion from aqueous solution.

MATERIAL AND METHODS

Three natural zeolites were obtained from Songkhla province. For the characterization of natural zeolite, the X-ray diffraction (XRD) patterns were acquired on a Philips X'Pert MPD, using CuK_α radiation source (λ=1.54 nm) at 45 kV and 35 mA. Each sample was measured in the range of $5° \leq 2\theta \leq 120°$ with scanning rate 0.04 2θ/sec at room temperature. The X-ray fluorescence (XRF) were performed on a Philips MagiX WDXRF. For water samples used in this study, the 10 ppm concentration of zinc stock solution was prepared in de-ionized water. To measure the exact concentrations of the metal ion before and after treatments by zeolite, atomic absorption spectroscopy (Perkin Elmer Model Analyst 800) was used.

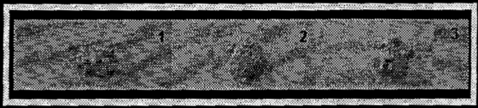

Figure 1. Natural zeolites from Songkhla province , no.1-3.

RESULTS

Structural Characterization of Natural Zeolites

In order to characterize the structure of three natural zeolites, XRD analysis was performed. The XRD pattern is shown in Figure 2. The obtained XRD patterns were compared with the patterns given in the ICDB number. The results reveal that the profiles correspond to Mordenite $((Na_2,Ca,K_2)Al_2Si_{10}O_{24}.7H_2O)$, Clinoptilolite $((Na,K,Ca)_5Al_6Si_{30}O_{72}.18H_2O)$ and Kaolinite-1Md $(Al_2Si_2O_5(OH)_4)$ compounds for natural zeolites no.1, no.2 and no.3, respectively. For XFR results, the elemental compositions of the zeolites were analyzed as reported in Table 1. It was found that the information obtained XRF analysis could support the structural data derived by the XRD pattern.

Applications of natural zeolites in the removal of zinc ion from aqueous solution

The optimal adsorption parameters was firstly determined. Mordenite was selected to use for the adsorption preliminary study. To study the effect of zeolite amount, mordenite was weighted and varied from 1.00, 1.50, 2.00, 2.50 and 3.00 g. Then, all suspension were carried out in 50 ml of each 10 ppm metal solution at pH 7.0. All batch adsorptions were performed for an hour. The removal efficiency of zinc ion from aqueous solutions is 49.67%, 59.16%, 67.62%, 75.58% and 79.97%, respectively. The result showed that 2.50 g of mordenite was optimum amount for the zinc adsorption. To study the effect of contact time for adsorption, the natural zeolite was weighted as the optimum amount obtained from from the previous step. Then, all suspension were carried out in 50 ml of metal solution at pH 7.0. All batch adsorptions were varied from 1, 2, 6, 12 and 24 hours, respectively. The zinc ion removal efficiency of 89.00%, 91.07%, 91.01%, 88.11% and 85.83% were derived, respectively. The optimum contact time for zinc adsorption is an hour. Therefore, an hour adsorption time and 50 g/l of the ratio of zeolite per water sample are chosen as optimal adsorption parameters for further step.

Consecutively, two natural zeolites, Clinoptilolite and Kaolinite-1MD were used as adsorbents for zinc ions removal from sample water based on adsorption parameters derived from the preliminary study. The results show that zinc ions were removed from aqueous solution with average removal efficiency of 86.06%, and 90.50%, respectively. The order of removal efficiency of zinc ions removal of three natural zeolites can be listed as Kaolinite-1MD ≈ Mordenite > Clinoptilolite.

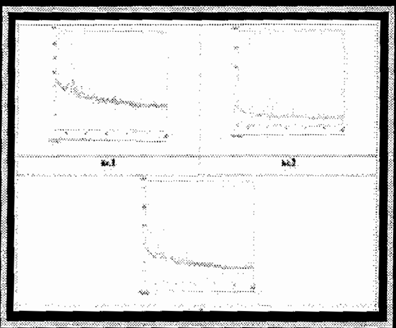

Figure 2. X-ray diffraction pattern of three natural zeolites, no.1-3.

Adsorption isotherms

The sorption data of zinc by the natural zeolite have been subjected to two sorption isotherms, namely, Freundlich and Langmuir isotherms to study the effect of initial metal ion concentration for adsorption behavior onto natural zeolite. Kaolinite-1MD was used as the highest effective adsorbent in this study. The results show that the Langmuir model effectively described the sorption data with high R^2 values (0.9999) compared with that obtained from Freundlich adsorption isotherm. It is clearly seen that Langmuir isotherms have a better correspondence with the experimental findings rater that Freundlich isotherm.

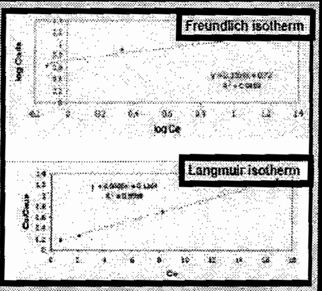

Figure 3. Adsorption isotherm for zinc ions on Kaolinite-1MD.

CONCLUSIONS

In summary, three Thai natural zeolites have been characterized and environmentally applied as effective adsorbents. The natural zeolites used show high adsorption capacities for zinc ion from aqueous solution. These findings show that both kaolinite-1MD and mordenite can be used as highly potential adsorbent for the removal of zinc ions from wastewater. For adsorption isotherms, Langmuir isotherms have a better correspondence with the experimental findings rather than with Freundlich isotherm. Based on the present study, it can be seen that the natural zeolites are effectively used for removing zinc ion from aqueous solution. These findings are beneficial information for practical applications in industrial wastewater treatment with high efficiency and relatively low cost materials.

ACKNOWLEDGEMENTS:
- Division of Research Promotion, Ubon Rajathanee University
- Faculty of Science, Ubon Rajathanee University

การวิเคราะห์โครงสร้างของซีโอไลต์ธรรมชาติด้วยเทคนิคเอ็กซ์เรย์ดิฟแฟรคชั่นและเอ็กซ์เรย์ฟลูออเรสเซ็นซ์และการประยุกต์ใช้ซีโอไลต์ธรรมชาติทางสิ่งแวดล้อมเพื่อการบำบัดไอออนของสังกะสีออกจากสารละลาย

STRUCTURAL CHARACTERIZATION OF NATURAL ZEOLITES BY USING X-RAY DIFFRACTION AND X-RAY FLUORESCENSE SPECTROSCOPY TECHNIQUES AND ITS ENVIRONMENTAL APPLICATIONS FOR REMOVAL OF ZINC ION FROM AQUEOUS SOLUTION

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บทคัดย่อ: ได้ทำการวิเคราะห์โครงสร้างของซีโอไลต์ธรรมชาติซึ่งเป็นสารดูดซับที่มีประสิทธิภาพจำนวน 3 ชนิด จากจังหวัดสงขลา โดยใช้เทคนิคเอ็กซ์เรย์ดิฟแฟรคชั่นและเอ็กซ์เรย์ฟลูออเรสเซ็นซ์ ผลจากการวิเคราะห์ด้วยวิธีเอ็กซ์เรย์ดิฟแฟรคชั่น พบว่าโครงสร้างของซีโอไลต์ธรรมชาติสอดคล้องกับ สารประกอบ Clinoptiolite Kaolinite-1MD และ Mordenite โดยมีสูตรโมเลกุลคือ $(Na,K,Ca)_5Al_6Si_{30}O_{72}.18H_2O$, $Al_2Si_2O_5(OH)_4$ และ $(Na_2,Ca,K_2)Al_2Si_{10}O_{24}.7H_2O$ ตามลำดับ และผลจากการวิเคราะห์ด้วยวิธีเอ็กซ์เรย์ฟลูออเรสเซ็นส์ ทำให้ทราบเปอร์เซ็นต์ของธาตุที่เป็นองค์ประกอบ ของซีโอไลต์นี้ซึ่งสามารถยืนยันข้อมูลทางโครงสร้างที่ได้จากวิธีเอ็กซ์เรย์ดิฟแฟรคชั่น จากนั้นได้ทำการศึกษาความ สามารถในการดูดซับได้ทำการศึกษาการประยุกต์ใช้ซีโอไลต์ธรรมชาติทั้ง 3 ชนิดนั้นในการบำบัดอิออนของสังกะสีออกจากน้ำตัวอย่างซึ่งเป็นการทดลองในระดับห้องปฏิบัติการ ในการศึกษาเบื้องต้นได้ใช้ Mordenite เพื่อหาพารามิเตอร์ที่เหมาะสมในการดูดซับ ผลการศึกษาพบว่าระยะเวลาที่เหมาะสมที่สุดในการแช่ซีโอไลต์ในน้ำตัวอย่างคือ 1 ชั่วโมง และจำนวนซีโอไลต์ต่อน้ำตัวอย่างที่เหมาะสมที่สุดคือ 40 กรัมต่อลิตร โดยมีปริมาณสังกะสี ที่ถูกดูดซับออกจากน้ำตัวอย่างมีค่าเฉลี่ยเป็น 76.09 % จากนั้นได้ใช้พารามิเตอร์ที่ได้นี้ในการศึกษาประสิทธิภาพในการดูดซับสังกะสี ของซีโอไลต์ธรรมชาติอีก 2 ชนิด ผลของการดูดซับของซีโอไลต์ธรรมชาติทั้งหมดเรียงลำดับได้ดังนี้ Kaolinite-1MD > Mordenite > Clinoptiolite พบว่าซีโอไลต์ธรรมชาติสามชนิดมีความสามารถในการดูดซับสังกะสี ในน้ำตัวอย่างได้ดีโดยประสิทธิภาพในการดูดซับเป็น 85.60%, 71.52% และ 63.06% ตามลำดับ ดังนั้นซีโอไลต์ทั้งสามชนิดเป็นตัวดูดซับที่สามารถนำมาประยุกต์ใช้ในการดูดซับสังกะสีจากน้ำทิ้งของโรงงานอุตสาหกรรม ซึ่งเป็นการลดค่าใช้จ่ายในการ

บำบัดน้ำเสียด้วยกระบวนการทางเคมีที่ใช้วัสดุราคาถูกที่พบมากในธรรมชาติและเป็นระบบที่รักษาสภาพ แวดล้อม

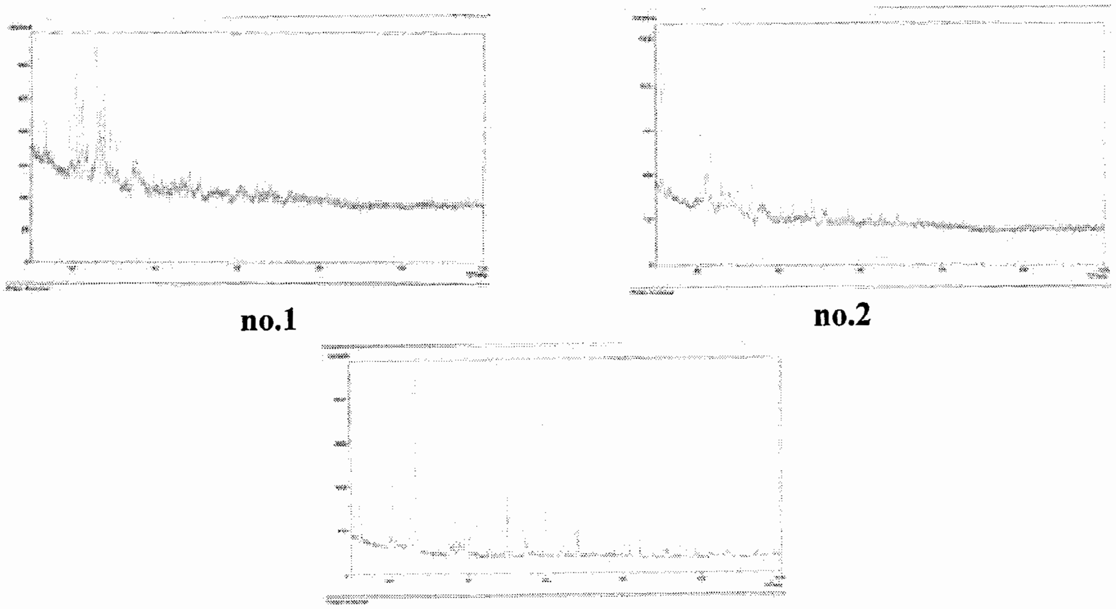
Abstract: Three natural zeolites found in the regions of Songkhla province, Clinoptiolite Kaolinite-1MD and Mordenite, have been applied to remove Zn^{2+} from aqueous solution, at laboratory scale. Mordenite was used for preliminary study of the adsorption parameters. An hour adsorption time and 40 g/l of the ratio of zeolite per water sample are optimum adsorption parameters with an average zinc ion removal efficiency of 76.09%. The optimum adsorption conditions were then used for other two natural zeolites. The results show that the effective removal sequence can be listed as Kaolinite-1MD > Mordenite > Clinoptiolite with Zn^{2+} removal efficiency of 85.60%, 71.52% and 63.06%, respectively. Kaolinite-1MD and Mordenite are successfully used to reduce potentially zinc ion from sample water. Accordingly, the natural zeolites are recommendable adsorbents for highly Zn^{2+} removal of industrial wastewater with low-cost treatment and environmentally friendly chemical processes.

Materials and Methods: Three natural zeolites, Clinoptiolite Kaolinite-1MD and Mordenite, as effective adsorbents, found in the Songkhla province were applied for zinc ion treatment from aqueous solution. For characterization of natural zeolites, the X-ray diffraction (XRD) patterns were acquired on a Philips X'Pert MPD, using CuKα radiation source (λ=1.54 nm) at 45 kV and 35 mA. Each sample was measured in the range of $5o \leq 2\theta \leq 120o$ with scanning rate 0.04 2θ/sec at room temperature. The X-ray fluorescence (XRF) were performed on a Philips MagiX WDXRF. For water samples used in this study, the 10.00 ppm concentration of Zn^{2+} solution was prepared by using Zn stock solution in de-ionized water. To measure the exact concentration of the Zn^{2+} before and after treatments by zeolite, atomic absorption spectroscopy (Perkin Elmer Model Analyst 800) was used.

Results, Discussion and Conclusion:

Part I Structural characterization of natural zeolites

In order to characterize the structure of three natural zeolites, XRD analysis was performed. The XRD pattern is shown in Figure 1. The obtained XRD patterns were compared with the patterns given in the ICDB number. The results reveal that the profiles correspond to Modernite ($(Na_2,Ca,K_2)Al_2Si_{10}O_{24}.7H_2O$), Kaolinite-1MD ($Al_2Si_2O_5(OH)_4$) and Clinoptiolite ($(Na,K,Ca)_5Al_6Si_{30}O_{72}.18H_2O$) compounds for natural zeolites no.1, no.2 and no.3, respectively. For XFR results, the elemental compositions of the zeolites were analyzed as reported in Table 1. It was found that the information obtained XRF analysis could support the structural data derived by the XRD pattern.



no.1

no.2

no.3

Figure 1. X-ray diffraction pattern of three natural zeolites, no.1-3.

Table 1. The element compositions of 3 natural zeolites, derived by XRF spectroscopy

Elements	Concentration (%)		
	no.1	no.2	no.3
O	49.47	50.32	50.80
Si	33.52	24.36	31.34
Al	6.726	4.829	15.18
Ca	4.405	7.857	0.1478
K	2.451	1.861	0.4484
Fe	1.394	0.8847	0.7995
S	1.003	9.140	0.06787
P	0.4226	0.3131	0.4590
Mg	0.3719	0.3153	<<
Ti	0.1810	0.1172	0.5987
Mn	0.05526	<<	-
Au	0.0000	0.0000	0.0000
Zr	0.0000	0.0000	0.0000
Sr	0.0000	0.0000	-
Rb	0.0000	-	0.0000
Se	0.0000	0.0000	0.0000
Y	<<	-	-

Part II Applications of natural zeolites in removal of Zn^{2+} from aqueous solution

As the Zn^{2+} efficiency was affected by adsorption time and ratio of zeolite usage per water sample volume, the optimal parameters for adsorption have to be determined. Modernite was selected to use for the adsorption preliminary study. The varying adsorption time with 30, 60, 90, 120, 150 and 180 mins. were performed and Zn^{2+} was removed from water samples with efficiency of 50.91%, 76.09%, 78.18%, 80.90%, 83.40% and 84.77%, respectively. The results show that the adsorption time is 60 mins. The ratio of zeolite per water sample volume with 20, 40, 60, 80 and 100 g/l were varied, resulting in zinc ion removal efficiency of 55.20%, 75.62%, 76.29%, 78.73% and 83.48%, respectively. The optimum ratio of zeolite per water sample volume is 40 g/l was obtained. Therefore, an hour adsorption time and 40 g/l of the ratio of zeolite per water sample are chosen as optimal adsorption parameters for further step.

Consecutively, 2 natural zeolites, Clinoptiolite and Kaolinite-1MD were used as adsorbents for Zn^{2+} removal from sample water based on adsorption parameters derived from the preliminary study. The results show that Zn^{2+} were removed from water samples with average removal efficiency of 63.06%, and 85.60%, respectively. The order of removal efficiency of Zn^{2+} removal of 3 natural zeolites can be listed as Kaolinite-1MD > Mordenite > Clinoptiolite. In summary, the fundamental study on zinc removal efficiency from aqueous solution at laboratory scale by using 3 natural zeolites as adsorbents were presented. Kaolinite-1MD and Mordenite show high adsorption capacities for Zn^{2+} in aqueous solution. These findings show that both Kaolinite-1MD and Mordenite can be used as highly potential adsorbent for the removal of Zn^{2+} from wastewater.

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