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ADSORPTION OF ANALCIME AND ZSM-5 ON METALS

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ABSTRACT

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<p>Natural zeolite with the basic cell structure of AlO_4 and SiO_4 tetrahedron has the ability of sewage purification. The way to adsorb in sewage is similar to activated carbon, and the zeolite has a good capacity of adsorption on cations.</p> <p>After modification, the activated zeolite acquires a better capacity of adsorption, cation-exchange and ion-exchange. After surfactant modification, zeolite can absorb the anions and organic compounds. In this way, zeolite can adsorb many kinds of ions in sewage.</p> <p>The aims of the thesis were: study the properties of natural zeolites; the adsorption capacity of analcime and ZSM-5 on metals and the theory of modification. In the experiment, the aim was to check out the adsorption capacity of Cu^{2+} and Ni^{2+} by using analcime and ZSM-5 and make a compare of the adsorption capacity between the cations in the same zeolite and between the zeolites in the same cations to find out which zeolite is better and in the same zeolite which cation was better adsorbed.</p> <p>The results of the experiment were that the Cu^{2+} cation was adsorbed better than Ni^{2+} in both analcime and ZSM-5. The adsorption speed of Cu^{2+} was faster than Ni^{2+}. ZSM-5 had a better adsorption capacity on both Cu^{2+} and Ni^{2+} than analcime, and the speed of absorbing was faster as well. In fact, during the experiment, there was an ion-exchange reaction, even though it took a small role of the experiment. The analcime and ZSM-5 contain alkali metal-sodium cation, so the ion-exchange process happen between Na^+ cation, Cu^{2+} and Ni^{2+} cations during the experiment.</p>		
Key words Analcime, ZSM-5, adsorption, natural zeolite, sewage, ion-exchange		

TABLE OF CONTENTS

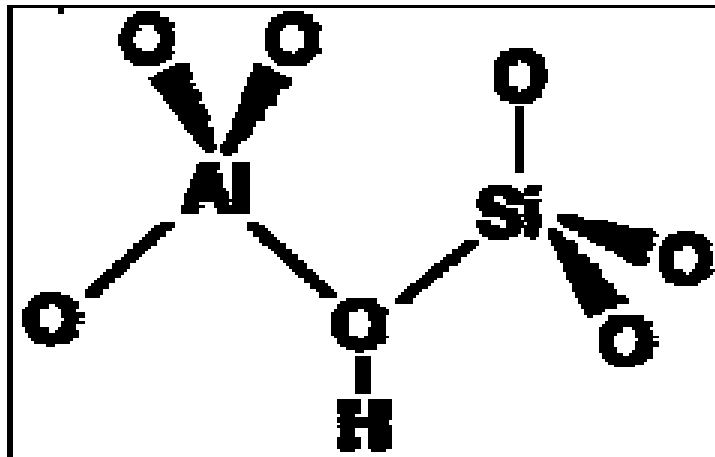
ABSTRACT

1 INTRODUCTION	1
2 PROPERTIES OF NATURAL ZEOLITES	4
2.1 The structure of natural zeolites.....	4
2.2 Ion-exchange property for natural zeolites.....	6
2.3 Ion-exchange selectivity property for natural zeolites	7
2.4 Adsorption capacity for natural zeolites	8
3 ANALCIME AND ZSM-5	10
3.1 Components and structure of analcime and ZSM-5.....	10
3.2 Properties of analcime and ZSM-5	12
3.3 The characteristics of analcime and ZSM-5.....	15
4 MODIFICATIONS OF NATURAL ZEOLITES AND ANALCIME.....	17
4.1 Activation processing of zeolites.....	17
4.1.1 Acid treatment and high-temperature calcinations.....	17
4.1.2 Salt and base method.....	18
4.2 Surfactant modification of zeolites	19
4.3 Ti and V modification method of analcime	20
4.4 Modification of ZSM-5 zeolite.....	21
5 APPLICATIONS OF NATURAL ZEOLITES FOR WATER TREATMENT.....	22
5.1 Adsorption capacity of natural zeolites for heavy metal ions	22
5.2 Adsorption capacity of natural zeolites for inorganic anions	25
5.3 Adsorption capacity of natural zeolites for ammonium.....	26
5.4 BET measurement theory	27
5.5 AAS measurement theory.....	27
6 EXPERIMENT TO DETERMINE ADSORPTION CAPACITY OF ANALCIME AND ZSM-5	29
6.1 Results of adsorption ability of analcime and ZSM-5	30
7 DISCUSSION AND CONCLUSIONS.....	35
REFERENCES	37
APPENDICES	

1 INTRODUCTION

Zeolites were found about 250 years ago. They are crystalline and micro porous minerals and distributed broadly in nature. Stilbite was found by the Swedish mineralogist Axel Fredrick Cronsted in 1756. Because he observed that during heating a large amount of steam engendered, the material was named “zeolite”. The meaning of the name is boiling stone which from the classic Greek word, where “zeo” is from “ζεω” means “to boil” and “lithos” is from “λιθος” means “stone”.

Zeolite is consist of silicon cation (Si^{4+}), aluminium cation (Al^{3+}) and oxygen anion (O^{2-}) which form the coordinating tetrahedral. This tetrahedral is a macromolecular that has uniform voids and channels created in crystals. The aluminium generates a positive charge in the polymer and can be located on oxygen anion which is connected to each aluminium cation as shown in Graph 1. (Jairo Antonio & Bagre 2005.)



GRAPH 1. Basic structure formula of a natural zeolite (adapted from Mumpton; Flanigen & Gottardi 1983)

In today's world, there is a serious shortage of clean water. Wastewater produced

by various industries is a main part of sewage in the world. Wastewater from the industrial processes can be discharged to land and water system. There are usually many poisonous and toxic substances such as cationic and anionic ions, oil and organics that can pollute the ecosystem and human health. Therefore, many techniques have been developed, and many technologies appeared for wastewater treatment in the past decades. Till now, adsorption is the accepted one that is a simple and effective way for water and wastewater treatment because of the development of an efficient adsorbent. Many adsorbents are found and used widely for adsorption of ions and organics in wastewater treatment such as activated carbon, clay minerals, biomaterials, zeolites and some industrial solid wastes, for example, sludge. (Shaobin & Yuelian 2009.)

Zeolitic tuffs are found in many places in the world after the first zeolitic mineral found in a volcanogenic sedimentary rock. Natural zeolites are used for many areas, such as adsorption, catalysis, building industry, agriculture and soil remediation. (Shaobin & Yuelian 2009.)

The bases of natural zeolites are hydrated aluminosilicate minerals that have a porous structure with many valuable physicochemical properties such as cation exchange, molecular sieving, catalysis and sorption. Because of zeolites' properties, the natural zeolites used for environmental applications are gaining new research interests. In water and waste water treatment, natural zeolites are considered a promising way in environmental cleaning process. Natural zeolites are being used till now for ammonium and heavy metal removal because of their properties of ion exchange. There are still other substances such as anions and organic compounds in water system, which natural zeolites and their modified forms can be used to remove. (Shaobin & Yuelian 2009.)

A concept of "molecular sieve" was proposed by McBain in 1932. His view is that zeolite is a kind of porous substance and the porous size can be changed to fit the

molecular size. Zeolite is a kind of molecular sieve, which is the most representative. (McBain 1932; Ping 2010.)

In the 1980s, the study and research of zeolites were not only remaining in the experimental stage; but also focus on new application. In Japan, natural zeolites are used for paper making, fertilizer and soil protection because of the advantages of natural zeolites. 90% of natural zeolites are used in construction areas, and about 9% are used in advanced industrial areas. (Flanigen et al. 2001.)

The aim of this thesis is to study the properties of natural zeolites, removal heavy metals from wastewater by using natural zeolites and comparing the adsorption capacity between analcime and ZSM-5. The research questions are the following: What are the types of zeolites (commercial and natural)? What are the applications of analcime? How the metal ions can be recovered by zeolites? (analcime vs. ZSM-5.). How can zeolites be used in water and waste water treatment? How the structure of natural zeolites can be modified?

In the experimental part, the work is to research the adsorption capacity of analcime and ZSM-5 for cations (eg. Zinc, Chromium and Phosphate). This experiment will show the adsorption capacity of cations by using analcime and commercial zeolite to find out which one is better and look into how the adsorption capacity of analcime and ZSM-5 for cations may vary.

2 PROPERTIES OF NATURAL ZEOLITES

Many kinds of natural zeolites are found in the world. Clinoptilolite, mordenite, phillipsite, chabazite, stilbite, analcime and laumontite are common forms to see. But the others, such as, offretite, paulingite, barrerite and mazzite, which are rare. (Shaobin & Yuelian 2009.)

2.1 The structure of natural zeolites

The most resourceful natural zeolite is clinoptilolite, which is also widely used in many areas. Their relatively independent components are found in zeolite structures, which are the aluminosilicate framework, exchangeable cations and zeolitic water. In general, the chemical formula of zeolite is $M_{x/n}[Al_xSi_yO_{2(x+y)}] \cdot pH_2O$ where M is (Na, Li, K) and /or (Ca, Mg, Ba, Sr), n is cation charge; $y/x = 1-6$, $p/x = 1-4$. (Ping 2010; Shaobin & Yuelian 2009.)

Zeolites can be divided into shelf, fibrous and flake structures based on the characteristics of zeolite minerals. According to the characteristics of zeolite pore systems, zeolites can be divided in one-dimensional, two-dimensional and three-dimensional. (Kallo 2001.)

The main body of the framework of natural zeolites is aluminum tetrahedron and silicon tetrahedron. In the central place of the tetrahedron are aluminum and silicon with four oxygen atoms in four vertices. Replaced Si^{4+} by Al^{3+} can form a negative charge of the tetrahedron framework and can attract the monovalent and divalent cations with water together. The most conserved and stable component is

aluminosilicate. The water molecules can be bonded to the exchangeable ions and framework ions by aqueous bridges in the voids of natural zeolites. The water forms bridges between exchangeable cations. The chemical formula and structure of important zeolites are showed below in Table 1. (Shaobin & Yuelian 2009.)

TABLE 1. Structural properties of some natural zeolites (Shaobin & Yuelian 2009)

Zeolite	Chemical composition (%)								CEC (meq/g)	Reference
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂		
Turkey clinoptilolite	70.90	12.40	1.21	2.54	0.83	0.28	4.46	0.089	1.6-1.8	[15]
Iranian clinoptilolite	70.00	10.46	0.46	0.2	-	2.86	4.92	0.02	-	[16]
Cuba clinoptilolite	62.36	13.14	1.63	2.72	1.22	3.99	1.20	-	-	[17]
Brazil mordenite	67.82	14.96	0.42	1.87	0.18	0.32	4.47	0.07	2.29	[18]
Italy phillipsite + chabazite	56.42	15.8	4.08	2.42	0.86	2.35	8.14	0.004	2.12	[19]
Turkey clinoptilolite	69.72	11.74	1.21	2.30	0.31	0.76	4.14	-	1.84	[20]
Chinese clinoptilolite	65.52	9.89	1.04	3.17	0.61	2.31	0.88	0.21	1.03	[21]
Chilean clinoptilolite + mordenite	67.00	13.00	2.00	3.20	0.69	2.60	0.45	0.20	2.05	[22]
Turkey clinoptilolite	69.31	13.11	1.31	2.07	1.13	0.52	2.83	-	-	[23]
Croatia clinoptilolite	64.93	13.39	2.07	2.00	1.08	2.40	1.30	-	1.45	[24]
Iranian clinoptilolite + mordenite	66.5	11.81	1.3	3.11	0.72	2.01	3.12	0.21	1.20	[25]
Turkey clinoptilolite	64.99	9.99	3.99	3.51	1.01	0.18	1.95	-	-	[26]
Chinese clinoptilolite	68.27	7.48	1.95	2.61	1.87	0.68	1.69	-	-	[27]
Turkey clinoptilolite	70.00	14.00	0.75	2.50	1.15	0.20	2.30	0.05	-	[28]
Chinese clinoptilolite	69.5	11.05	0.08	2.95	0.13	2.95	1.13	0.14	-	[29]
Ukrainian clinoptilolite	67.29	12.32	1.26	3.01	0.29	0.66	2.76	0.26	-	[30]
Ukrainian mordenite	64.56	12.02	0.95	3.58	0.68	0.94	2.03	0.23	-	[30]
Slovakian clinoptilolite	67.16	12.30	2.30	2.91	1.10	0.66	2.28	0.17	-	[31]
Croatian clinoptilolite	55.80	13.32	1.30	5.75	0.70	3.90	2.35	-	-	[32]
Ukraine clinoptilolite	66.7	12.3	1.05	2.10	1.07	2.06	2.96	-	0.64	[33]
Australian clinoptilolite	68.26	12.99	1.37	2.09	0.83	0.64	4.11	0.23	1.20	[34]

The cation that in the extra framework has a weak bonding can be removed or exchanged easily by a strong solution with another cation. The basic CEC (cation exchange capacity) of a zeolite is the replacement between Al and Si in the tetrahedron framework. The more amounts of Al, the more amounts of cations are needed to balance the charge of the tetrahedron. The CEC of the natural zeolite is about 2 to 4milli equivalents/g (meq/g), which is twice more than bentonite clay. The natural zeolites differ from the most noncrystalline ion exchangers such as organic resins or inorganic aluminosilicate gels. They have selectivity toward competing ions. The cations in the high strength-field hydration sphere can prevent them from approaching to the place of charge in the framework, so most cations have low strength-field. The cations can be held tightly and exchanged selectively by the zeolite. The analcime, for example, has a relatively low CEC, which is about 2.25meq/g, the selectively cations are Cs > Rs > K > NH₄ > Ba > Sr > Na > Ca > Fe > Al > Mg > Li. (Frediric 1999.)

The structure of zeolite is crystal. The diameter of pore of zeolite is 0.3 to 0.7 nanometers (larger than the diameter of a water molecule). The property can be used to adsorb and filter molecules when the diameters of the molecules are smaller than the pores. Hence, the molecules can be screened from the mixture and that is called molecular sieving. (St. Cloud Zeolite Mining Company 2010; Ping 2010.)

2.2 Ion-exchange property for natural zeolites

One characteristic of zeolite is ion-exchange, which can exchange cations and anions with external medium. The ion-exchange functions in the isomorphous fashion. The following equation describes the equilibrium of ion exchange:



Where Z_A^+ and Z_B^+ are the valences of each cation. L is a part of the zeolite framework holding unit, which is negative charge. (Shaobin & Yuelian 2009.)

The behavior of ion-exchange depends on many factors such as framework structure, charge density and ion shape of the anionic framework, ionic charge and concentration of the external electrolyte solution. Because of the different environmental situations, there are many kinds of chemical composition of natural zeolites, and different cation exchange capacity (CEC) abilities. Table 1 below shows the chemical composition and cation exchange capacity (CEC) of different kinds of natural zeolites. The CEC values are between 0.6 to 2.3 meq/g as can be seen from Table 1. (Shaobin & Yuelian 2009.)

The frame of anionic charge can affect the maximum CEC. But it does not mean

the zeolites have the same ion-exchange ability when they have the common framework. Some zeolites have different ability of ion-exchange even though they have the same framework, and the ability is based on the Si/Al ratio. The cation in the zeolite structure can be fastened in a right position. In different spatial locations, the performances of cations are different. In the ion-exchange process, the reaction rates can be controlled through the diffusion velocity. Because of their characteristics, natural zeolites play a role as an inorganic ion exchange agent in environmental protection. Zeolites can be used to treat industrial sewage which contains heavy metal cations and anions, and radioactive sewage. (Curkovic, Cerjan-Stefanovic & Filipan 1997; Ping 2010.)

2.3 Ion-exchange selectivity property for natural zeolites

In the ion-exchange process, a few amounts of metal can be exchanged into the zeolites easily, but other non-metals cannot be exchanged or exchanged after metal cations exchanging. Because of the amount of metals can be exchanged by zeolites easily, the ionic exchange process of zeolite has selectivity. Ion exchange selectivity can be affected by factors such as the zeolite crystal structure, the cation properties (ionic radius and hydration energy) and the ion-exchange situations. (Semmens & Seyfarth 1978; Ping 2010.)

The hydration free energy of cation exchange and the radius of hydrated cations are mostly the factors which affect to the high Si/Al ratio of the selectivity of cations of zeolites. In other words, the low Si/Al ratio depends on the crystal ionic radius of cations and the electrostatic attraction size between the zeolites anion positions and the cations. (Semmens & Seyfarth 1978.)

Because of ion-exchange conditions such as the temperature, pH and concentration ion-exchange selectivity can be changed. As seen from Table 2, the monovalent cations are better than the divalent cations of selectivity ability.

TABLE 2. The selective ability of heavy metals ion-exchange comparison (adapted from Wang, Feng, Gu & Wu 2006; Ping 2010)

Zeolite	Selectivity series
Analcime	$Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$
Mordenite	$Cs^+ > Rb^+ > K^+ > NH^+ > Na^+ > Li^+$
Chabazite	$Ti^+ > K^+ > Ag^+ > Rb^+ > NH_4^+ > Pb^{2+} > Na^+ > Ba^{2+} > Sr^{2+} > Ca^{2+} > Li^+$
Clinoptilolite	$Cs^+ > Rb^+ > NH_4^+ > K^+ > Na^+ > Li^+$ (alkali metal) $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ (alkaline earth metal)

2.4 Adsorption capacity for natural zeolites

One of good adsorbents in wastewater treatment is activated carbon used for the sewage containing heavy metals. In the removal of heavy metals from the wastewater area, commercial zeolites are found working more efficiently and cheaper than the activated carbon. By decreasing the particle size of zeolite, the zeolites can improve the performance of the zeolite adsorption, but finer particles in the column can reduce the permeability in the waste water treatment. (Yong, Jae, Seon, Jung & Young et al. 2006.)

Because the generation of the commercial zeolite is expensive, mixtures of zeolites and some cheaper organic and inorganic materials (such as fly ash, clays,

polymers and Portland cement) are used instead of the commercial zeolites for the specific pollutants to reduce the cost of materials. Portland cement is one of the most common materials which are known by its solidification and stabilization. In the mixture, it is used to supplement zeolite adsorption purpose. (Yong, Jae, Seon, Jung & Young et al. 2006.)

Zeolites have the characteristic of a high adsorption capacity at the lower partial pressure and higher temperature of, because of the electric field in the cavities and polar actions of zeolites. In the process of adsorption, one common factor is the size of zeolite pore, but there are other factors as well such as the molecules of polarized groups or the molecules containing polar groups, which can react with the surface of zeolite strongly. The reason why the zeolites have this characteristic is that the zeolite itself is also a kind of polar substance. A strong partial positive charge is given by a cation in the electrostatic induction way can polarize the polarized molecule or attract the negative polar molecule in center. When the polarity is stronger or molecules can be polarized more easily, zeolite can adsorb more susceptibly. There is a strong affinity between zeolite and H₂O molecule, because the H₂O molecule is a strong polar molecule. (Gunter & Zanetti 2000.)

3 ANALCIME AND ZSM-5

Analcime or also can be called analcite (from the Greek, means “weak”) is a kind of grey, white or colorless tectosilicate mineral as GRAPH 2 shows below,



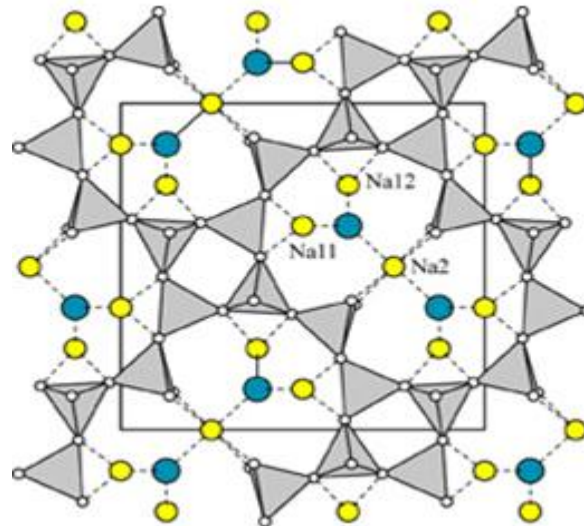
GRAPH 2. Analcime from analcime basalt. (Photo: Paleonet 2006)

3.1 Components and structure of analcime and ZSM-5

There are hydrated sodium aluminum silicates which exist in cubic form in crystalline in analcime. The chemical formula of analcime is $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$. A

small amount of potassium and calcium are in the analcime. Silver-bearing synthetic variety exists as well, but the main part is sodium. The structure and chemical properties are more similar to the feldspathoids, even though they are classified to the zeolite mineral. The analcime can be found in the analcime basalt and other alkaline igneous rocks. It also can be found in prehnite, calcite and zeolite as the cavity and vesicle fillings (Cornelius.S. & Cornelis 1985.).

It was a milestone in zeolite mineralogy that Taylor (1930) determined the structure of analcime. Because it is not only the first solved zeolite structure, but also the basis to definition a new zeolite structure which is based on the discovery of the $(\text{Si}, \text{Al})\text{O}_4$ tetrahedron framework arrangement. Around the tetrad screw axes, there is a singly-connected 4-rings arranged in chains in the framework of analcime. 4_1 and 4_3 screw axes are alternated and they are parallel chains. Each parallel chain is linked to the crystallographic axe and each 4-ring is a part of three mutually perpendicular chains. Each cage contains Na-cations and water molecules interconnect chains and in the location of T-site, it acts as a bridge connecting 3 cages. The Si and Al distribution is random, because the T-site in the cubic space group is equal to the others. In the centre of the cages there are Na-cations (yellow in the graph) and in a unit of cell there are 24 cages. Hence, the Na-cations (generally 16, but can be 12 to 17) also distribute randomly in the cages, and water molecules (blue in the graph) occupy in the 16 sites randomly as well. (Colella, de'Gennaro & Aiello 2001.) There is a unit of cubic model of analcime as can be seen from GRAPH 3.



GRAPH 3. A unit of analcime in cubic form (Photo:Commission on natural zeolites)

There is an idealized unit cell of $\text{Na}_{16}\text{Al}_{16}\text{Si}_{32}\text{O}_{96} \cdot 16\text{H}_2\text{O}$ (Meier, Olson & Baerlocher 1996) and it is widespread product of low-temperature hydrothermal activity. (Amethyst Galleries' Mineral Gallery 2006; Ping 2010.)

ZSM-5 zeolite is used in the process of conversion and production as the adsorbent. The ZSM-5 zeolite is divided into aluminosilicate zeolite normally. In the ZSM-5 zeolite, the pentasil units groups are the main parts, and they are linked by the oxygen atoms which are act as the bridge. One pentasil unit is composed by eight five-rings linked together. Normally the Al or Si atom is on the top of the eight rings and can be bonded by oxygen. (Lermer, Draeger, Steffen and Unger 1985.)

3.2 Properties of analcime and ZSM-5

Analcime exists in nature in different types, and the properties also differ with other kinds of natural zeolites. There are some macroscopic and microscopic properties

to realize analcime. Table 3 shows the detailed properties of analcime. (Mineral Data Publishing 2001.)

TABLE 3. Analcime Properties (adapted from Mineral Data Publishing 2001; Ping 2010)

Physical properties	
Mineral group	Zeolite mineral
Color	Clear, white or gray, with greenish, yellowish
Luster	Vitreous
Transparency	Crystals are transparent to translucent
Hardness	5 ~ 5.5
Specific gravity	2.24 ~ 2.29
Refractive index	$n = 1.479 \sim 1.493$
Fusibility	3.5

Chemical component			
Chemistry	NaAlSi ₂ O ₆ ·H ₂ O, Hydrated Sodium Aluminum Silicate		
Unit cell chemical formula	Na ₁₆ Al ₁₆ Si ₃₂ O ₉₆ ·16H ₂ O		
Variable component	Si/Al = 1.8 ~ 2.8; H ₂ O = 14 ~ 18		
Crystallographic data			
Symmetry	Cubic	Space group	Ia3d
Structure type	ANA	Cell volume	2.590Å ³
Density	2.25 g/cm ³	Unit cell constant	a = 13.723 ~ 13.733Å

Structure properties	
Density of framework	1.85 g/cm ³

Pore opening	2.6Å
Maximum CEC	4.9 meq/g

It is more important for ZSM-5 zeolite to have not only Si^{4+} and Al^{3+} ions, but also other cations in its framework owing to its good catalytic performance and structure properties. The iron cations are provided that can be exchanged into ZSM-5 zeolites; the cations like iron cations other than Si^{4+} and Al^{3+} can fine-tuning the acidic sites strength and form bifunctional groups. Based on this property, the ZSM-5 zeolite can be modified the cavities and fit the shape selectivity better; and the modified ZSM-5 also can increase the concentration of Al^{3+} ions in the framework to prevent the transition temperature transporting from monoclinic to orthorhombic phase. The lowest Si/Al ratio known is 10, but there are some other cations found instead Al^{3+} in the framework to fit different situation. (Vetrivel, Pal & Krishnan 1991.) There are some ratios known below in TABLE 4.

TABLE 4. Different Cations' ratio in ZSM-5 zeolites (adapted from Vetrivel, Pal & Krishnan 1991)

X/Y	Lowest ratios
Si/Al	10
Si/Ti	67.5
Si/Fe	36
Si/B	16.1
Si/Ga	10.7
Si/Ge	2

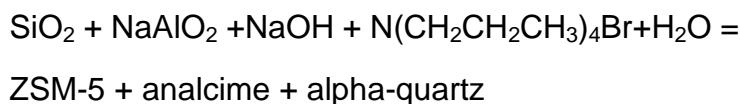
3.3 The characteristics of analcime and ZSM-5

Barrer (1950, 2342-2350.) found two characteristics in analcime ion-exchange, so that analcime can be used as an ion-sieve. One of the characteristics is that the analcime can exchange ions at room temperature. When the temperature increases, the ion-exchange occurs more easily. The reason is that there are smaller pores in analcime. (Barrer & Hinds 1953.) Barrer and Hinds found that, when the transition metals were exchanged by sodium-analcime, the amount of siliceous zeolites was increased; on the other side, Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} ions were less favored in exchanging with sodium. When a pair of cations exchange with analcime, the preference of analcime depends on the size of the cations, the lower framework charge (high Si/Al) prefers the large cation and the higher framework (low Si/Al) prefers the smaller cation. K, Ti, Rb, NH_4 and Ag were reported in the ion exchange isotherms with analcime by Barrer and Hinds. It was hard for very small Li^+ to exchange with analcime because of its high energy of hydration in solution. Barrer and Hinds also found that K^+ , Ag^+ , Tl^+ , NH_4^+ and Rb^+ cations were very easy to be exchanged by Na-analcime at high level of temperature; but only small amount of Sr, Mg, Co and Ni can be exchanged by Na-analcime. (Sudaporn, Kunwadee & Alan, 2004.) The other characteristic is that the hysteresis phenomenon can easily appear in the ion exchange process. (Barrer & Hinds 1953.) Analcime was found to be potentially used in the disposal of storage and titrated water by Dyer and Yusof (1987, 196; 1989, 129) after researching extensively on cations.

The ZSM-5 zeolite usually plays a role of a catalyst. By using organic silica, the ZSM-5 zeolite can be synthesized. The diameter of the pores in ZSM-5 is increased by 2 times and the range of diameter is augmented to 1500 Å from 5 Å. ZSM-5 also has other advantages such as stable thermal, flexibility and certain shape selectivity. Depends on these advantages, ZSM-5 zeolites are widely used in the

catalyst and molecular sieve area. (Viswanadham, Kamble, Singh, Kumar and Dhar 2008.)

The reaction of preparing ZSM-5 is:



The conditions under the reaction are high temperature and pressure. (Pelriae, Treaton.N.J 1978.)

It was found that cobalt is a very good catalyst in some typical reactions; one of the reactions is Co over ZSM-5 zeolite, and this seems to be the best one in the reactions. The Co-ZSM-5 zeolites have other good characteristics as well, including high activities, high selectivity on linear hydrocarbons and low activities in the water-gas shift reaction. Hence, the Co-ZSM-5 zeolite is one of the best catalysts for the Fischer-Tropsch synthesis (FTS) through the natural gas conversion. The Co-ZSM-5 is moreover used in the autoxidation of alkanes and alkylaromatics reactions. (Pierella, Saux, Fernández García, Bercoff & Bertorello 2002.)

4 MODIFICATIONS OF NATURAL ZEOLITES AND ANALCIME

Activated zeolite is formed through a variety of special processes of natural zeolites activation.

4.1 Activation processing of zeolites

Because zeolites can be activated, there should be a new CEC (cation exchange capacity) adsorption capacity. Activated zeolites have a better process of ion exchange performance. Many kinds of contaminants in sewage can be removed by activated zeolites. To some extent, the performance of activated zeolite is similar or better than activated carbon, and the cost is lower than that of activated carbon. Activated zeolite can be formed in many ways such as acid, base or salt treatments and high-temperature calcinations. The hybrid method can make the activation of zeolite more efficient than others. (Xing, Ding & Feng 2000, Ping 2010.)

4.1.1 Acid treatment and high-temperature calcinations

In the acid medium, the zeolite structure cannot be damaged because of the good acid resistance in natural zeolite. But cation such as Na^+ , K^+ can be exchanged by hydrogen. The hydrogen ion in the activated zeolite can be bounded via the heavy metal cation when the zeolites and heavy metal ions occur ion-exchange. (Xing et al. 2000; Ping 2010.)

The first aim of acid treatment is to remove the impurities and substances from the cavities and pores of zeolite such as Fe_2O_3 . The second purpose is to make more effective space, so that the large radius of cations such as Ca^{2+} , Mg^{2+} and Na^+ , can be displaced by H^+ , and this is called proton exchange. But there is also a disadvantage in the dealumination and reduction of thermal stability of acid treatment. (Xing et al. 2000.)

The temperature is normally controlled between 350°C to 580°C in the calcination method in the air atmosphere. The time is from 90 minutes to 120 minutes. The purpose of high temperature calcinations is to remove the impurities so that the cavities and pores are empty in zeolite. (Xing et al. 2000.)

Kurama, Zimmer and Reschetilowski (2002, 301-305) reported that the natural Turkish clinoptilolite was modified into H-form in two methods. The first one was ammonium ion exchange (NH_4^+) by using the high temperature calcinations, and the other method was using the acid method directly with HCl. The data showed that through the acid method, the surface area and pore volume of clinoptilolite were increased. The volumes of pores were increased to 0.25 from 0.13 ml/g and the surface areas were increased from 35 to 315 m^2/g . (Ping 2010.)

4.1.2 Salt and base method

Because the Ca^{2+} and Mg^{2+} can be exchanged by K^+ , NH_4^+ and Na^+ , the salts NaCl, KCl and NH_4Cl can be used in the salt treatment generally. Curkobic et al. (1997, 1379-1382) compared the effect of lead and chromium by using natural zeolites and activated zeolites, which were treated by NaCl. The data showed that the NaCl-activated zeolites' ion exchange capacity and removal efficiency of lead and

chromium were increasing. NaOH solution is generally used in the base treatment. Hu, Wang and Shao (1997, 5-6) reported that natural zeolites were treated in the NaOH solution. When the concentration of NaOH was 3-5 mol/L, the process temperature was at $95 \pm 5^\circ\text{C}$ and the ratio of liquid-solid was 3.5: 1, the activated zeolites had a good adsorption of Cr^{3+} , Cd^{2+} and Pb^{2+} . (Ping 2010.)

4.2 Surfactant modification of zeolites

The AlO_4 tetrahedron part with a negative charge in the zeolite can exchange cations. The adsorption capacity of natural zeolites for anions and organic compounds is poor in the solution. Therefore, the surface properties should be changed. Organic surfactants are used as one modification method. The surfactant modified zeolite (SMZ) can adsorb anions, cations and non-polar organic molecules which are in aqueous solutions. There are some common surfactants that have been used in the natural zeolite modification: cetyltrimethyl ammonium (CTMA), hexadecyltrimethyl ammonium bromide (HDTMA), octadecyldimethylbenzyl ammonium (ODMBA), n-cetylpyridinium (CPD) benzyltetradecyl ammonium (BDTDA) and stearyldimethylbenzyl ammonium (SDBAC). (Wang & Peng 2009; Ping 2010.)

The cationic organic surfactants have hydrophilic and hydrophobic properties as well. The surfactant molecules in low concentration conditions can start to form micelle in the solvent, which is called critical micelle concentration (CMC). (Bowman 2003.)

The hydrophilic group or the hydrophobic tail group can bring the molecules into water. When the positive charge group or the hydrophobic group is trying to prevent

the molecules from dissolving into water, the molecules can be arranged on the surface of a zeolite. Hence, there will be a “monolayer” or “hemimicelle” directly on the surface of a zeolite. When the adsorption reaches the maximum point, the surfactant concentrations are higher than the critical micelle concentration (CMC). Hence, the surfactant molecules cannot concentrate on the surface of zeolite any more. (Haagerty & Bowman 1994.)

The hydrophobic group has a characteristic which is hydrophobic interaction. The hydrophobic group can do its best to get away from water condition under this characteristic. In this solution condition, the activated molecules on the surface are self-polymerization and take shape to an “admicelle” or “bilayer”. Therefore, SMZ are built by complex functional groups for positively charged exchange sites formed by the positive groups $-NR^+$. (Wang & Peng 2009; Ping 2010.)

4.3 Ti and V modification method of analcime

Through incorporating Ti or V, the synthetic analcime can be modified. The starting material selected was Egyptian kaolin. The ways such as XRD (X-Ray diffraction), SEM (scanning electron microscope), EDX (energy dispersive X-Ray), ESR (electron spin resonance), TGA (thermal gravimetric analysis) and DSC (differential scanning calorimetry) were used to test the ability of removal of Cu^{2+} , Ni^{2+} and Pb^{2+} of the modified analcime, and the results showed that the modified analcime could remove the ions well. Under investigation, the preference towards to the heavy metal ions depends on the amount of Ti and V used. When the amount of Ti and V increases, the size of analcime crystal was decreased. (Hegazy, Maksod & Enin 2010.)

4.4 Modification of ZSM-5 zeolite

The Si/Al atomic ratio of ZSM-5 can be decreased significantly by using 0.8M sodium carbonate and 0.01M sodium hydroxide aqueous solution. The sodium orthosilicate and its dimer, sodium pyrosilicate are removed from the ZSM-5 zeolite framework selectively. The diameter of micropores is 0.49 nm, which are much smaller than the original micropores after desilication process. The ion-exchange activity of ZSM-5 zeolite is much higher than the parent one, because of its increasing density of Al tetrahedral sites. (Van Mao, Le, Ohayon, Caillibot, Gelebart & Denes 1997.)

5 APPLICATIONS OF NATURAL ZEOLITES FOR WATER TREATMENT

As the development of industrialization and urbanization increasing, the water pollution is increasing. Environment is damaged greatly by the sewage. And water pollution includes heavy metals, inorganic and ammonia contaminants. In recent years, many scientists have tried to find out the low-cost and metalloid mineral adsorbents. Zeolite is a good choice because of the unique structure. Zeolite has good ion exchange and adsorption properties and can save much money.

In the past few decades, zeolite has been used widely in controlling urban and industrial sewage as ion exchange agents, adsorbents, molecular sieves, agriculture and horticulture because it has special physical and chemical properties. Based on these applications, however, the most common way to use zeolite is the wastewater treatment, and the zeolite plays a role on adsorption and ion exchange.

5.1 Adsorption capacity of natural zeolites for heavy metal ions

The ions Na^+ , K^+ and Ca^{2+} are the most suitable cations to remove the heavy metal cations in the industrial wastewater because the exchangeable ions cannot damage the environment. One usage of natural zeolite adsorption is to remove the radioactive strontium (^{90}Sr) and cesium (^{137}Cs) in the sewage. It is easy for zeolite to remove the ions Ba^{2+} , Cd^{2+} , Ni^{2+} , Zn^{2+} and Pb^{2+} , even though the methods of experiment and industry are different. (Ouki & Kavanagh 1999.)

Panayotoval (2001, 267-272) modified the Bulgarian natural zeolites to remove the

heavy metals and used in several experiments as well. To remove Ni^{2+} ions, the natural zeolites were modified by the acid method or base method with the solution of NaOH, NaCl, HCl or CH_3COONa in a batch process. The natural zeolites worked in the first order irreversible reactions in the uptake process following the Langmuir adsorption isotherm, which could describe the uptake equilibrium well. The adsorption capacity could be increased 25% - 30% by CH_3COONa and NaCl when adsorb Ni^{2+} cation.

The natural zeolites, modified by NaCl, CH_3COONa and NaOH, have a characteristic that they can raise the adsorption capacity in the adsorption of Cu^{2+} . Natural zeolites are modified by salt and base to adsorb Cu^{2+} and precipitate copper have almost the same effect. There is not much impact when the ions Ca^{2+} and Mg^{2+} both exist in the solution during the adsorption. (Panayotoval 2001.)

In the second order of irreversible reactions, the kinetic equation can describe the adsorption of Cu^{2+} ion well in the uptake process using natural zeolite. In the adsorption of Cd^{2+} , the equation shows the kinetics and thermodynamics both in the uptake process by using both natural and modified zeolites. The best way to describe is the Freundlich adsorption isotherm from data. The amount of Mg^{2+} and Ca^{2+} are reduced in the process of adsorption of Cd^{2+} - and NaCl - and CH_3COONa -modified zeolites have higher ability of uptake. (Panayotoval 2000.)

Zheng, Wang and Zhang (1998, 24-25) tested the adsorption of nickel from wastewater by using natural zeolites. They tested the amount of zeolites and nickel ratio, the wastewater pH and the efficiency of the reaction. The experiment showed that, under the condition of $\text{pH} \geq 4$ and $\text{Ni}^{2+} \leq 100\text{mg/L}$ and mass ratio of nickel/zeolite is 1: 800, the efficiency of Ni^{2+} removing is more than 99%. (Ping 2010.)

The natural zeolite with the formula $\text{Na}_{15.04}[\text{Al}_{15.04}\text{Si}_{32.96}\text{O}_{96}] \cdot 16\text{H}_2\text{O}$ in the crystal

form called analcime can be used to remove Ag^+ ions in the aqueous solution. Seryotkin (2000, 265-269) reported the studies of Ag exchange by analcime. The items studied were the analcime crystal size, the duration of first order treatment, second order treatment, temperature for both orders and the methods used to measure results. In the experiment, the size of analcime crystal was 0.20-0.25mm, the ratio of $\text{Ag}^+ : \text{Na}^+$ was 100: 1 in the 4N- AgNO_3 solution used in the first order treatment. The duration time and temperature were two weeks and 145°C , then the samples after the first order were washed by hot distilled water in autoclave with 24 hours at 140°C . The ways to measure the results were both thermogravimetry (TG-50, TA 3000, Mettler.) up to 850°C and the weight loss during 1 hour burning at 900°C , in order to form $16\text{H}_2\text{O}$ in each unit. Therefore, the formula of Ag-analcime can be presented as $\text{Ag}_{15.04}[\text{Al}_{15.04}\text{Si}_{32.96}\text{O}_{96}] \cdot 16\text{H}_2\text{O}$. The data showed that the discrepancy in Al populations was $\Delta \leq 0.04$ and for Ag-analcime was 0.04-0.06 due to the refinement uncertainties.

Tangkawanit (2005, 171-175) worked on the selectivity series for Pb, Cu, Ni and Zn with analcime. He studied the ion exchange of Cu^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} with analcime (ANA). The analcime was produced from an economically available Thai perlite. The ions Pb^{2+} , Cu^{2+} , Zn^{2+} and Ni^{2+} were added into the Na-analcime. The results showed that the selectivity of Na-analcime to the ions was $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$, the enthalpy of cation hydration determined the selectivity of zeolites.

Alvarez-Ayuso, Garcilla-Sanchez & Querol (2003, 4855-4862) studied the adsorption capacity ability of natural clinoptilolite and synthetic (NaPI) zeolite on the ions of Cr (III), Ni (II), Zn (II), Cu (II) and Cd (II) in order to consider the clinoptilolite purification ability on the removal heavy metal ions in the sewage. The concentrations and the solid/liquid ratios of the metal ions in solution ranged from 10 to 200 mg/l and 2.5 to 10 g/l respectively. The Langmuir model was a good way to describe all sorption processes and measured metal sorption sequences. The studies showed that the sorption capacity of synthetic zeolite ($b_{\text{Cr}} = 0.838$ mmol/g,

$b_{Ni} = 0.342$ mmol/g, $b_{Zn} = 0,499$ mmol/g, $b_{Cu} = 0.795$ mmol/g, $b_{Cd} = 0.452$ mmol/g) was 10 times better than the natural clinoptilolite ($b_{Cr} = 0.079$ mmol/g, $b_{Ni} = 0.034$ mmol/g, $b_{Zn} = 0,053$ mmol/g, $b_{Cu} = 0.093$ mmol/g, $b_{Cd} = 0.041$ mmol/g).

5.2 Adsorption capacity of natural zeolites for inorganic anions

Cheng prepared modified natural zeolites, which modified by the cationic surfactant Bromohexadecyl pyridine (CPB) and hexadecyltrimethyl ammonium bromide (HDTMA) to treat Cr (VI) sewage. The results showed that the efficiency of treating Cr (VI) wastewater by using CPB is 4-5 times faster than using HDTMA. Under the ideal condition of the CPB method to modify the natural zeolites, the concentration of CPB was 1.5%, the temperature was 25 °C and time was 36 hours. The best condition of using CPB method with modified natural zeolites to treat the Cr (VI) wastewater was 30 minutes and the temperature was 25°C during the adsorption; the mass of modified natural zeolite was 2g, the component of sewage contained Cr (VI) was 50 mg/l in 25 ml. The result was that the rate of removal Cr (VI) can reach 90% or more. (Cheng 2005; Ping 2010.)

Zhang, Cui and Xiao (1999, 116-120) reported that the adsorbents of activated natural zeolites had a good performance on the removing of phosphorus with the capacity of 15 mg/g or more in the wastewater. Li, Xiao and Yu (1994, 173-176) investigated that the fluoride ions can be absorbed by modified natural zeolite less than 1 mg/l and water hardness and alkalinity can also be reduced.

5.3 Adsorption capacity of natural zeolites for ammonium

Ammonia-nitrogen can exist in water in two forms: One is free ammonia (NH_3) and the other one is ammonium ion (NH_4^+). The substance of ammonia-nitrogen comes in two sources; one is from industrial sewage such as monosodium glutamate wastewater and coal carbonization wastewater, and the other one is from the urban wastewater. Mostly ammonia-nitrogen comes is from the decomposition of proteins in water, but sometimes is from the nitrite nitrogen and nitrate nitrogen conversion. When the concentration of ammonium in water is high, the oxygen dissolving ability of water is decreased and the condition leads to be toxic for the aquatic organism. Ammonia can be adsorbed by zeolites easily, because ammonia is a polar molecule, and its size is less than the pore and cavity of zeolites. (Tang, Wu, Shu and Liu 2006.)

Zhao and Sun (2001, 385-388) reported that the experiment of low concentration of NH_4^+ removed by natural zeolites in water. The items they studied were natural zeolite particle size, initial concentration of NH_4^+ and pH, the concentration of renewable liquid Na^+ and the flow velocity. There was only a small amount of NH_4^+ removed, but the natural zeolites can regenerate and used for recycling for 18 times repeatedly, the exchange capacity of NH_4^+ ion was only 4% less than before. Based on the characteristics, the natural zeolites were used in the deamination industry to remove the microscale NH_4^+ . (Ping 2010.) Zhang, Wen and Wu (1999, 14-17) reported that there was a good effect on the treatment of removing ammonia-nitrogen with NaCl-natural zeolite regeneration in the sewage.

The regeneration methods used to adsorb NH_4^+ are: chemical, calcinations regeneration and bio-renewable. The zeolites, which have been used to remove NH_4^+ , can be treated again with NaOH and NaCl solutions to replace NH_4^+ ions. The bio-renewable method is to use bacteria to nitrify NH_4^+ ions to take them out of

zeolites and form to nitrate. The calcinations regeneration method is that roasted the zeolites by a range of temperature between 300-600°C to change the NH_4^+ to NH_3 . (Abd El-Hady, Grunwald, Vickova & Zeithammerova 2001; Ping 2010.)

5.4 BET measurement theory

BET theory was first presented by Stephen Brunauer, Paul Hugh Emmett and Edward Teller in 1938. "BET" comes from the first letter of their family names. They used this theory to explain the molecule adsorption in a solid surface, and now this measurement is one of the basic methods to analyze the substance adsorption. (Brunauer, Emmett & Teller 1938.) Using the BET measurement, the samples can be analyzed in the surface and porosity field. In the vacuum chamber situation, the adsorbate particles can be adsorbed both onto the surface and into the internal porous. The gas adsorbate particles' pressure is measured to determine the adsorption isothermal in the chamber. Then the adsorption isothermal can be used to determine the volume of the gas in the chamber and the gas adsorbents can form a monolayer on the particle surface. (Malvern 2011.)

5.5 AAS measurement theory

The AAS measurement is a more and more popular and important way to measure the substance particle size in the past few years. Laser diffraction can be used to measure the particle size through the light scattering and refraction when the laser beam comes onto the particles, but it does not mean laser diffraction can measure the particle size distribution. The higher refractive index the particles have, the

more light can be scattered. (Wedd 2003.)

6 EXPERIMENT TO DETERMINE ADSORPTION CAPACITY OF ANALCIME AND ZSM-5

The experiment is to measure the adsorption capacity of analcime and commercial zeolite in the experimental work by using aqueous solutions with Cu^{2+} and Ni^{2+} , and compares the adsorption capacity of analcime and ZSM-5 zeolites in order to find out which one is better under the same condition.

Firstly, the analcime was washed in a 500 ml beaker by distilled water and filtered in vacuum. Secondly, the analcime was dried in the oven at $110\text{ }^{\circ}\text{C}$ and left it in the oven for one day to make it as dry as possible.

The standard Cu^{2+} and Ni^{2+} aqueous solutions were prepared with a concentration of 15 ppm for each aqueous solution in the volumetric flasks. The tested aqueous solutions of Cu^{2+} and Ni^{2+} were prepared as well in the concentration series of 5, 10, 15 ppm in 100 ml volumetric flasks.

The 300 ml aqueous solution of Cu^{2+} with concentration of 15 ppm was put into the 500 ml Erlenmeyer flask, and stirred with a magnetic stirrer with a speed of 250 rpm. Then the analcime with a mass of 3 g was put into the Erlenmeyer flask and recorded the time. The samples of 5 ml were taken at 0, 2, 5, 10, 30, 60 and 180 minutes by using 5 ml volumetric pipettes. The samples was vacuum filtered and put into test tubes.

6.1 Results of adsorption ability of analcime and ZSM-5

Cations of Ni^{2+} and Cu^{2+} were already adsorbed by analcime and ZSM-5 separately at 0, 2, 5, 10, 30, 60, 180 minutes. The concentrations of the solutions after adsorbing were measured by AAS. The goal was to determine the amount of cations which the cations were absorbed by analcime and ZSM-5 at different time. TABLE 5 shows the analysis of Ni^{2+} and Cu^{2+} cations concentration by analcime.

TABLE 5. Ni^{2+} and Cu^{2+} concentration analyzed by analcime

The cation of Ni^{2+}			
Time [min]	Test [ppm]	Absorbed part [ppm]	Absorbed percent [%]
0	4.88	$15 - 4.88 = 10.12$	$10.12/15 * 100\% = 67.47$
2	4.11	$15 - 4.11 = 10.89$	$10.89/15 * 100\% = 72.60$
5	3.64	$15 - 3.64 = 11.36$	$11.36/15 * 100\% = 75.73$
10	3.20	$15 - 3.20 = 11.80$	$11.80/15 * 100\% = 78.67$
30	2.95	$15 - 2.95 = 12.05$	$12.05/15 * 100\% = 80.33$
60	2.87	$15 - 2.87 = 12.13$	$12.13/15 * 100\% = 80.87$
180	2.07	$15 - 2.07 = 12.93$	$12.93/15 * 100\% = 86.20$
The cation of Cu^{2+}			
Time [min]	Test [ppm]	Absorbed part [ppm]	Absorbed percent [%]
0	3.79	$15 - 3.79 = 11.21$	$11.21/15 * 100\% = 74.73$
2	3.10	$15 - 3.10 = 11.90$	$11.90/15 * 100\% = 79.33$
5	2.39	$15 - 2.39 = 12.61$	$12.61/15 * 100\% = 84.07$
10	1.74	$15 - 1.74 = 13.26$	$13.26/15 * 100\% = 88.40$
30	0.60	$15 - 0.60 = 14.40$	$14.40/15 * 100\% = 96.00$
60	0.27	$15 - 0.27 = 14.73$	$14.73/15 * 100\% = 98.20$
180	0.26	$15 - 0.26 = 14.74$	$14.74/15 * 100\% = 98.27$

And TABLE 6 shows the analyzing of Ni^{2+} and Cu^{2+} cations concentration by

ZSM-5.

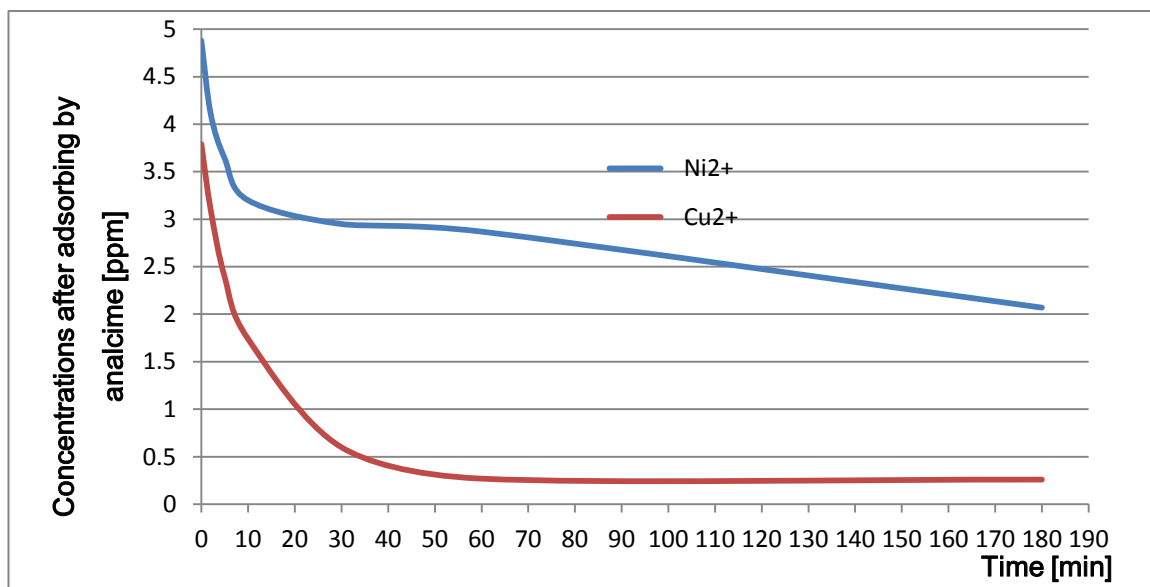
TABLE 6. Ni²⁺ and Cu²⁺ concentration analyzed by ZSM-5

The cation of Ni ²⁺			
Time [min]	Test [ppm]	Absorbed part [ppm]	Absorbed percent [%]
0	4.76	15 – 4.76 = 10.24	10.24/15 * 100% = 68.27
2	4.04	15 – 4.04 = 10.96	10.96/15 * 100% = 73.07
5	2.92	15 – 2.92 = 12.04	12.04/15 * 100% = 80.27
10	1.79	15 – 1.79 = 13.21	13.21/15 * 100% = 88.07
30	1.47	15 – 1.47 = 13.53	13.53/15 * 100% = 90.20
60	1.06	15 – 1.06 = 13.94	13.94/15 * 100% = 92.93
180	1.06	15 – 1.06 = 13.94	13.94/15 * 100% = 92.93
The cation of Cu ²⁺			
Time [min]	Test [ppm]	Absorbed part [ppm]	Absorbed percent [%]
0	1.90	15 – 1.90 = 13.10	13.10/15 * 100% = 87.33
2	0.46	15 – 0.46 = 14.54	14.54/15 * 100% = 96.93
5	0.38	15 – 0.38 = 14.62	14.62/15 * 100% = 97.47
10	0.20	15 – 0.20 = 14.80	14.80/15 * 100% = 98.67
30	0.11	15 – 0.11 = 14.89	14.89/15 * 100% = 99.27
60	0.10	15 – 0.10 = 14.90	14.90/15 * 100% = 99.33
180	0.10	15 – 0.10 = 14.90	14.90/15 * 100% = 99.33

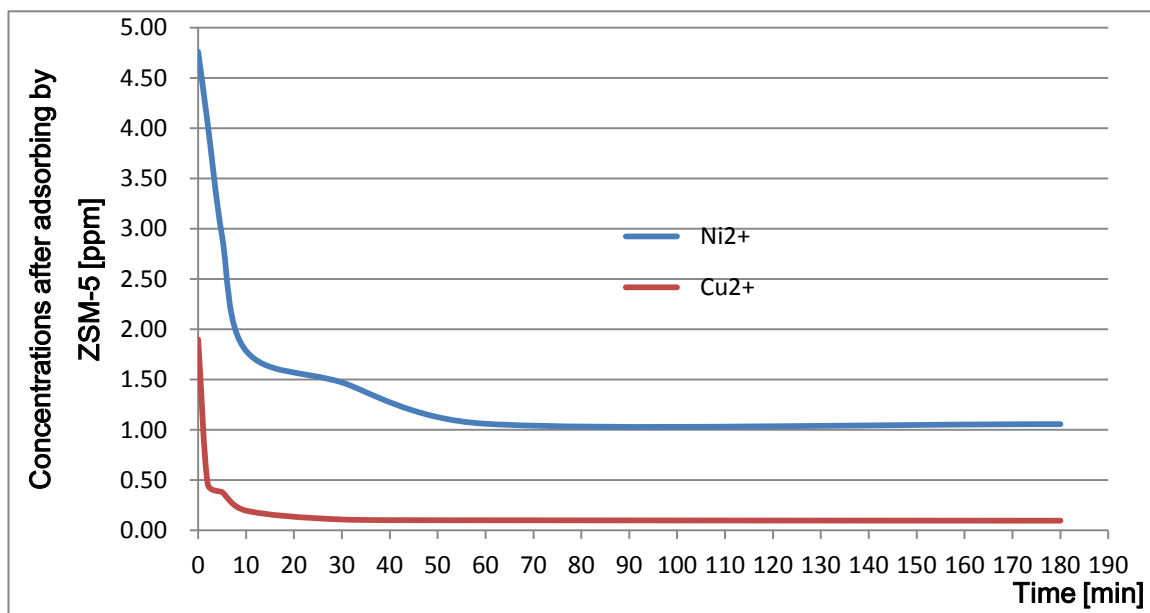
As the analysis shows, the maximum adsorption percent of nickel and copper from analcime are 86.20% and 98.27%, and the maximum adsorption percent of nickel and copper from ZSM-5 are 92.93% and 99.33%. The data shows that the ability of adsorption of ZSM-5 is much greater than that of analcime, both on copper and nickel cation, and after 60 minutes, the concentration of cations change a little. In ZSM-5, the concentrations of nickel and copper cations are the same.

The adsorption ability of Cu^{2+} and Ni^{2+} by analcime and ZSM-5 is shown by the following GRAPH 4 and GRAPH 5.

GRAPH 4. Concentration of Cu^{2+} and Ni^{2+} after adsorption by analcime



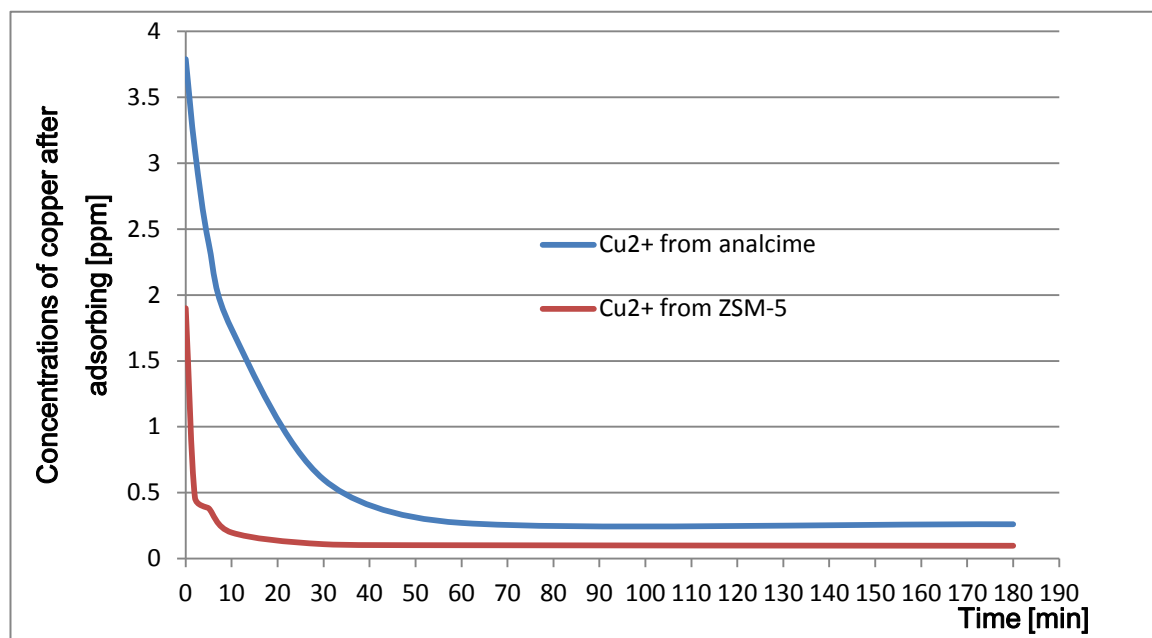
GRAPH 5. Concentration of Cu^{2+} and Ni^{2+} after adsorption by ZSM-5



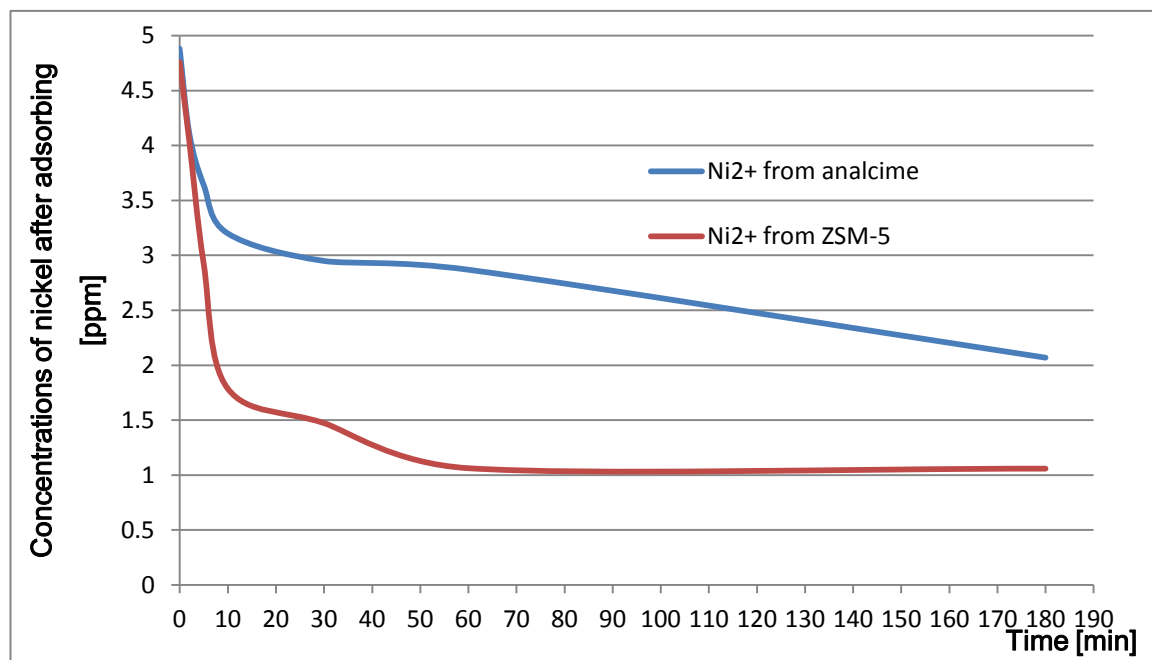
From GRAPHS 4 and 5, it can be seen that the both adsorption abilities of analcime and ZSM-5 of copper ion are better than that of nickel ion. The following GRAPH 6 and GRAPH 7 below show that the adsorption ability between analcime and ZSM-5

on the same ion cation Cu^{2+} and Ni^{2+} separately.

GRAPH 6. Concentrations of Cu^{2+} in analcime and ZSM-5



GRAPH 7. Concentrations of Ni^{2+} in analcime and ZSM-5



From GRAPH 6 and GRAPH 7, it can be seen that the adsorption ability of Cu^{2+} and Ni^{2+} of ZSM-5 is much better than that of analcime. Cu^{2+} and Ni^{2+} of ZSM-5 are

more rapidly adsorbed than that of analcime, especially copper in 2 minutes, the concentration from 15ppm drop to 0.46ppm. But after 10 minutes, the adsorption level of copper is very small. Even though the adsorption level of copper from analcime is changed more slowly, finally the adsorption ability is closed to that from ZSM-5. The Ni^{2+} cation adsorbed by ZSM-5 is also greater than that by analcime. The nickel cation is adsorbed by ZSM-5 rapidly between 0 to 10min, but the adsorption level change to be smaller after 50 minutes adsorption. But the nickel cation adsorbed by analcime changes quickly in the first 10 minutes, and then keeps changing till to the end of the process. The adsorption ability of ZSM-5 and analcime on Ni^{2+} cation are different. At the end of point of the concentration of nickel cation from ZSM-5 and from analcime, it can be seen clearly that the ZSM-5 has much greater adsorption ability than analcime.

Ion-exchange can affect the adsorption of analcime and ZSM-5 as well. The ion exchange selectivity series shows that the selectivity ability of Cu^{2+} is better than Ni^{2+} both in analcime and ZSM-5. Thus the copper cation in the aqueous can be exchanged more easily and quickly than nickel cation.

7 DISCUSSION AND CONCLUSIONS

The purposes of studies are the properties of natural zeolite, analcime and ZSM-5, the adsorption ability of analcime and ZSM-5. The experimental part of the work is to measure the adsorption capacity of analcime and ZSM-5 on Cu^{2+} and Ni^{2+} cations. The purpose of the experiment was to compare the ability of analcime and ZSM-5 on the same cation and the adsorption capacity difference between Cu^{2+} and Ni^{2+} cations, in order to find out which cation is easier to be absorbed.

The experiment shows that the adsorption ability of ZSM-5 is greater than analcime of the same cation. The adsorption efficiency of Cu^{2+} is better than Ni^{2+} both in ZSM-5 and analcime. When the adsorption happens, there is another reaction which is ion-exchange. The cations can exchange Na^+ in analcime and Si^{4+} in ZSM-5. The main process is adsorption and the by-reaction is ion-exchange. Cu^{2+} and Ni^{2+} can exchange Na^+ and Si^{4+} in the ion-exchange process. The cages in ZSM-5 also have positive effects on the adsorption of cations. Another reason why the adsorption ability of Cu^{2+} is better than Ni^{2+} is that the radius of copper cation is smaller than nickel cation. (Barrer & Hinds 1953.)

Because zeolite cannot adsorb all the cations, modification is used to form activated zeolite to complete this situation. (Xing, Ding & Feng 2000.) The modification can also improve the adsorption ability and capacity of zeolite. After adsorption, zeolite can be recycled. In this way, it saves materials and protects environment and it is called renewable resource. Natural zeolite also has a high efficiency, and it is an inexpensive material for wastewater treatment. Because of the characteristics of zeolite, it is used for sewage treatment in many countries and also has a promising application prospect. (Shaobin & Yuelian 2009.)

Even though zeolite has many advantages on sewage treatment, there are also some disadvantages. Zeolite has a high adsorption level on polarity water; hence the adsorption capacity of NH_4^+ and Pb^{2+} is smaller. Therefore, to increase the capacity of NH_4^+ and Pb^{2+} , the H_2O adsorption level should be reduced. (Gunter & Zanetti 2000.) There is another disadvantage of zeolite, which is the toxic content in zeolite. The toxic content, such as Pb, Hg, of zeolite should be measured first and removed, even though it is very low, or it will be a new polluted source when using. (Ping 2010.)

Nowadays, zeolite has a considerable application prospect on the adsorption of the sewage treatment. In many countries, it is used in factories and studied in laboratories. Modifications of zeolite are being developed including reducing the amount of raw materials and improving the modification efficiency by many countries. Zeolites will play a more and more important role as the time goes.

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Calculations of preparing 15 ppm standard solutions

Prepared 15 ppm for each Ni^{2+} and Cu^{2+} solutions by using $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 1L.

Prepared 15 ppm solution contains Ni^{2+} in 1L.

$$15 \text{ ppm} = 15 \text{ mg/L}$$

$$m_{\text{Ni}} = 15 \text{ mg/L} \cdot 1\text{L} = 15 \text{ mg}$$

$$M_{\text{Ni}} = 58.6934 \text{ g/mol}$$

$$M_{\text{S}} = 32.065 \text{ g/mol}$$

$$M_{\text{O}} = 15.9994 \text{ g/mol}$$

$$M_{\text{H}} = 1.00794 \text{ g/mol}$$

$$M_{\text{NiSO}_4 \cdot 6\text{H}_2\text{O}} = 262.86 \text{ g/mol}$$

$$58.6934 \text{ g/mol} / 262.86 \text{ g/mol} = 15 \text{ mg} / m_{\text{NiSO}_4 \cdot 6\text{H}_2\text{O}}$$

$$m_{\text{NiSO}_4 \cdot 6\text{H}_2\text{O}} = 67.1779 \text{ mg}$$

Prepared 10 ppm standard solution contains Ni^{2+} in 90 ml from 15 ppm standard solution.

$$15 \text{ ppm} / 10 \text{ ppm} = 90 \text{ ml} / V_{15 \text{ ppm}}$$

$$V_{15 \text{ ppm}} = 60 \text{ ml}$$

Prepared 5 ppm standard solution contains Ni^{2+} in 90 ml from 15 ppm standard solution.

$$15 \text{ ppm} / 5 \text{ ppm} = 90 \text{ ml} / V_{15 \text{ ppm}}$$

$$V_{15 \text{ ppm}} = 30 \text{ ml}$$

Prepared 15 ppm solution contains Cu^{2+} in 1L.

$$15 \text{ ppm} = 15 \text{ mg/L}$$

$$m_{\text{Cu}} = 15 \text{ mg/L} * 1\text{L} = 15 \text{ mg}$$

$$M_{\text{Cu}} = 63.546 \text{ g/mol}$$

$$M_{\text{S}} = 32.065 \text{ g/mol}$$

$$M_{\text{O}} = 15.9994 \text{ g/mol}$$

$$M_{\text{H}} = 1.00794 \text{ g/mol}$$

$$M_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}} = 249.685 \text{ g/mol}$$

$$63.546 \text{ g/mol} / 249.685 \text{ g/mol} = 15 \text{ mg} / m_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}$$

$$m_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}} = 58.938 \text{ mg}$$

Prepared 10 ppm standard solution contains Cu^{2+} in 90 ml from 15 ppm standard solution.

$$15 \text{ ppm} / 10 \text{ ppm} = 90 \text{ ml} / V_{15 \text{ ppm}}$$

$$V_{15 \text{ ppm}} = 60 \text{ ml}$$

Prepared 5 ppm standard solution contains Cu^{2+} in 90 ml from 15 ppm standard solution.

$$15 \text{ ppm} / 5 \text{ ppm} = 90 \text{ ml} / V_{15 \text{ ppm}}$$

$$V_{15 \text{ ppm}} = 30 \text{ ml}$$