LITERATURE REVIEW

Phosphorus from wastewater is one pollutant that has an effect on the environment and humans. Phosphorus is a major source of eutrophication - algal bloom- (Henri, 1996). Therefore, scientists attend to eliminate phosphorus from water source in order to prevent eutrophication water pollution.

Definition of phosphorus

Phosphorus is the 15th element in the periodic table. It has five valence electrons: three solitary and one doublet. It forms three covalent bonds involving the solitary electrons and one can predict that this atom should be able to form a semipolar bond by doublet exchange. This possibility is perfectly illustrated by the phosphorus anhydride molecule (P_2O_5) (Henri, 1996).

The P_2O_5 molecule reacts with water to orthophosphate acid form:

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$$

This triacid can undergo successive ionization to yield the ions:

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \quad \text{with } pK_1 = 2.16$$

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \quad \text{with } pK_2 = 7.16$$

$$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+ \quad \text{with } pK_3 = 12.40$$

The pH-dependent partitions of total phosphate among these four forms are as shown in Figure1.

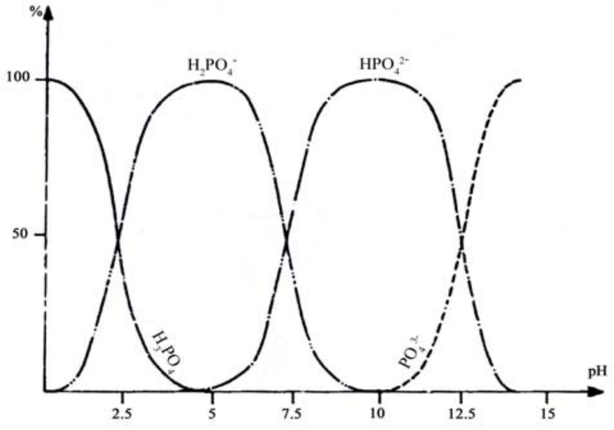


Figure 1 pH-dependent variation of phosphorus speciation.
Source: Henri (1996)

Role and importance of phosphorus in pollution

Phosphorus is responsible for nearly all of the pollutant compounds presented in domestic or urban wastewaters. Approximately 50% to 70% of wastewater phosphate compounds are in orthophosphate form, the balance being polyphosphates and organic phosphorus compounds (Henri, 1996). Because polyphosphates and organic phosphorus compounds are hydrolyzed as they pass through a biological treatment plant, so the phosphorus present in the effluent is 90% orthophosphate form (Henri, 1996). The various sources of these compounds in municipal wastewaters are shown in Table1.

Table 1 The sources of phosphorus compounds in municipal wastewaters

sources	quantity (g/person-equivalent)
Metabolic contributions	1.5
Food preparation and cooking	0.3
Detergents	2.1 to 2.3

Source: Henri (1996)

Phosphorus removal

1. Biological phosphorus removal

Microorganisms are used to remove phosphorus in wastewater. Biological processes are configured to encourage the growth of bacteria with the ability to take up and store large amounts of inorganic phosphorus. Due to biomass having a specific gravity slightly greater than water, the biomass can be removed from wastewater by gravity settling.

Biological treatment is the traditional method of phosphorus removal. Biological phosphorus removal in an activated sludge system is caused by bacteria (Subramanial and Arnot, 2001), which are able to store phosphate intracellularly as polyphosphate. The bacterial cells consume polyphosphate by changing it into the form of orthophosphate. There utilize polyphosphate as an energy source and the excreted orthophosphate leaves the system or can be stripped from the biomass. The biomass is retained inside the reactor behind the anaerobic membranes and the resulting high sludge ages losing the potential benefit of a high efficiency of phosphorus released as solids can cause fouling, and reduction in membrane flux.

In conventional sludge activation process (Fresenius *et al*., 1989), the mechanical stage of conventional mechanical-biological systems can reduce phosphorus concentration in fresh sludge from about 15 to 20 mg-P/L to about 10 to 15 mg-P/L and in the joining biological stage i.e. activation or biological filter system, to about 5 to 10 mg-P/L.

There are combination uses of microorganisms and adsorbent to increase the capability of phosphorus removal. Hrenović *et al*. (2003) investigated the influence and performance of the addition of support material on the orthophosphate uptake in a pure culture of *A. calcoaceticus*, and addition of natural zeolite or clay in the aerobic phase resulted in a significantly higher final efficiency of phosphate removal. The amount of phosphate removed depended on particle size and type of material used.

To eliminate phosphorus by algae, the process is to combine the oxidation trench containing an algal activated sludge mixture and a subsequent precipitation stage with the addition of a precipitation reagent such as sodium hydroxide and calcium hydroxide. In this process, the phosphate concentration can be reduced to about 0.6 to 0.9 mg-P/L.

As a result of biological treatment of phosphate, phosphate concentration is reduced mainly by its storage into biological cell mass. It makes phosphate elimination depend on intricate conditions such as pH, temperature, and oxygen dissolved in water, which are optimum conditions for bacterial growth.

Even though phosphorus removal by biological treatment reduces chemical costs and lessens sludge production as compared to chemical precipitation, it has a longer time for treatment of wastewater than chemical precipitation. Moreover, the phosphorus removal by biological treatment is difficult and complicated operation.

2. Chemical phosphorus removal

Phosphorus is removed from wastewater using chemical reagents, for example, aluminum, calcium, and iron salts, to precipitate phosphorus. The phosphate precipitates are insoluble and flocculates aid removal of suspended matter.

Chemical treatment is the chemical precipitation of phosphorus by the addition of the salts of multivalent metal ions that form precipitates of sparingly soluble phosphate.

In ion exchange, Jorgensen (1973) used a new wastewater treatment system examined on a pilot plant scale. Approximately 400 g of calcium hydroxide, 100 g of bentonite and 1 g polyflocculant were used in ion exchange process per m^3. This was followed by an ion exchange process on a weak base anion exchanger removing phosphate and nitrate.

In the coagulation process, experiments were conducted by Simmonds (1973) to determine the efficiency of phosphate removal. Aluminium sulphate was used in coagulation tests. The coagulation experiments were conducted to determine the efficiency of phosphate removal. The study was performed on different samples of sewage with different initial concentrations of phosphate. The results indicated that, after the initial coagulation requirement of the sewage had been satisfied, these were a requirement for precipitation of aluminium phosphate. Boisvert *et al.* (1997) used aluminium sulphate (alum) and poly-aluminium-silicate-sulphate (PASS) for coagulation of phosphate. The results indicated that phosphate ion binding by alum and PASS where the interaction involved H^+ or OH^- transfer depended on the pH range 5-7. In some conditions, low pH, size of PO_4 ions and the resistance to shear stress, PASS was found better than alum for coagulation. Akay *et al.* (1998) used red mud as a coagulant in crossflow microfiltration. The results shown that the colloidal red mud particles could coagulate phosphate ions. Seida and Nakano (2002) studied phosphate removal using layered double hydroxides containing iron. Iron-based layered double hydroxides were synthesized, consisting of Mg^{2+}, Ca^{2+}, Fe^{3+} ions. When cations and/or hydroxides were released, it worked effectively as a coagulant for the phosphate removal. Özacar and Şengil (2003) used polyelectrolytes, tannin (natural polyelectrolyte) and AN913 (synthetic anionic polyelectrolyte), and clay in coagulation/flocculation processes for water treatment. The results found that alum was the most effective coagulant at all phosphate concentrations. Adding clay, tannin and AN913 significantly increased phosphorus removal efficiency and addition of coagulants significantly decreased the required alum dose.

3. Physicochemical phosphorus removal

Physicochemical removal is a process to co-eliminate phosphorus removal from wastewater by physical and chemical treatment. Methods are used to eliminate contaminants such as adsorption, ion exchange, ultrafiltration, reverse osmosis, and electrodialysis.

There are many ion exchangers that are used for phosphate removal. Gregory and Dhond (1972) studied anion exchange equilibria involving phosphate, sulphate, and chloride. They investigated different anion exchange resins in order to determine their applicability in the removal of phosphate from wastewater. All synthetic ion exchange resins consisted of a polymeric matrix with chemically bound ionic groups throughout the resin structure. There found the ability of phosphate adsorption on their surface related to the type of functional group. Moreover, Liberti *et al.* (1979, 1981, and 1986) used Kestel as a strong base anion resin to removed phosphate. The results found an average phosphate removal of more than 95%. In 1998, Zhao and Sengupta used a new class of sorbent, referred to as polymeric ligand exchanger (PLE), to remove phosphate from contaminated wastewater. Their works showed strong evidence that the PLE was very selective toward phosphate, chemically stable, and also amenable to efficient regeneration.

Wastewater is the one pollution which has effect on the environment and a human. Wastewater from domestic or urban has elements- phosphorus, carbon, and nitrogen- which they are responsible for nearly the entire pollutant compound (Henri, 1996). Domestic wastewater is produced by plant workers, shower facilities, and cafeterias. The statistic of human using the tap water to consume in Bangkok and other provinces are about 440 and 150 liters per person per day respectively (Udomsinrod, 1996). Therefore, in the city will be has effluence and the tendency of wastewater pollution higher than in the country.

The physical characteristics of domestic wastewater have the odor of freshly turned earth. Fresh sewage is gray color but septic sewage is black color. Septic sewage is considerably more offensive to the olfactory nerves. It is rotten egg odor of hydrogen sulfide and the mercaptans. In general, the temperature of the wastewater will be higher than the water supply normally by 10 - 20°C. This is because of the addition of warm water from households and heating within the plumbing system of the structure.

Due to the number of chemical compounds found in wastewater are almost limitless, so chemical characteristics normally restricting its consideration to a few general classes of compounds three typical compositions of untreated domestic wastewater were summarized in Table 2. The pH of these wastewaters will be in the range of 6.5 to 8.5. Industrial wastewater composition may be significantly different from domestic wastewater.

Table 2 Typical composition of untreated domestic wastewater

Constituent	Weak	Medium	Strong
	(all mg/L except settle able solids)		
Alkalinity	50	100	200
BOD_5	100	200	300
Chloride	30	50	100
COD	250	500	1,000
Suspended solids (SS)	100	200	350
Settle able solids, ml/L	5	10	20
Total dissolved solids (TDS)	200	500	1,000
Total Kjedahl nitrogen (TKN)	20	40	80
Total organic carbon (TOC)	75	150	300
Total phosphorus (as P)	5	10	20

Source: Machenzie and David (1991)

Domestic effluents generally contain elevated phosphorus concentration, largely as orthophosphate, which is then discharged to surface waters. The problems created when phosphorus is discharged to surface water well known and largely involve accelerated eutrophication such as lake, ponds, and reservoirs. Recently, the scientists have demonstrates an adsorption to pollution treatments (such as Liu Ruixai *et al.,* 2002). Therefore, adsorption is an interesting method to study.

Definition of surface and interfaces

The term *surface* is the outer boundary of an artifact or material layer. It is an area in which the properties vary from those of one phase to those of the connecting phase. This transition occurs over distances of molecular dimensions at least. *Interface* is the point of interconnection between two distinct but adjacent communications systems having different function.

General definition

Some of the principal terms and properties associated with adsorption and porous solids were defined in Table 3 and Table 4, respectively.

Table 3 Definitions: adsorption

Term	Definition
Adsorption	Enrichment of one or more components in an interfacial layer
Adsorbate	Substance in the adsorbed state
Adsorbent	Solid material on which adsorption occurs

Table 3 Definitions: adsorption (Cont'd)

Term	Definition
Chemisorption	Adsorption involving chemical bonding
Physisorption	Adsorption without chemical bonding
Surface coverage	Ratio of amount of adsorbed substance to monolayer capacity
Monolayer capacity	Ether chemisorbed amount required to occupy all surface sites or physisorbed amount required to cover surface

Source: Rouguerol *et al.* (1999)

Table 4 Definitions: porous solids

Term	Definition
Porous solid	Solid with cavities or channels
Open pore	Cavity or channel with access to the surface
Closed pore	Cavity not connected to the surface
Pore volume	Volume of pores determined by stated method
Pore size	Pore width (diameter of cylindrical pore or distance between opposite walls of slit)
Porosity	Ratio of total pore volume to apparent volume of particle
Surface area	Extent of total surface area as determined by given method under stated conditions
External surface area	Area of surface outside pore
Internal surface area	Area of pore walls

Source: Rouguerol *et al.* (1999)

From Table 3, the term *adsorption* is the enrichment of one or more of the components in the region of surface or interface between two phases. In any solid or liquid, atoms at the surface are subject to unbalanced forces of attraction normal to the surface plane. These forces are merely extensions of the forces acting within the body of material and are ultimately responsible for the phenomenon of adsorption.

Investigation into adsorption should provide information concerning the amount of a substance which can be adsorbed on a surface, the influence of pressure and temperature on this amount, and the strength of the adsorption bond. Investigation should also reveal the changes which the adsorbing surface and the adsorbed particles undergo as a result of adsorption, and desorption should be given of the condition of the orbital which take part in the adsorption bond.

Researchers have used different materials as adsorbent for eliminating phosphorus. Liu Ruixai *et al.* (2002) studied the adsorption properties, including adsorption rate, adsorption isotherm, and effect of solution conditions on adsorption, of phosphate, fluoride, and arsenate onto a newly developed ion exchange fiber, that was polyacrylonitrile fiber. They found that the adsorption properties of the ion exchange fiber for three anions depended on the pH value and anion concentration. The adsorption percentage of phosphate was more than 99% in the pH range of 3.0 to 5.5 (Liu Ruixai *et al.*, 2002). This study used the Freundlich model to describe the adsorption equilibrium data. The adsorption of phosphate on the ion exchange fiber was a rapid process. Adams *et al.* (1987) studied the adsorption of phosphate by soils. The soil used in that experiment was treated by extraction with oxalate, citrate and dithionite, and sodium hydroxide. Barrow (1984) studied the effect of pH on phosphate adsorption by soils. The effect of pH on phosphate adsorption differed between soils. For unfertilized soils, increase in pH up to about 5.5 decreased adsorption. For fertilized soils, measured adsorption increased with pH. Clark *et al.* (1997) used sand, activated carbon, peat-moss, zeolite, compost, cotton milling waste product and a chemically-modified agrofiber for filtration of pollutants. Phosphate adsorption was also measured in all the media. It was found that the compost filter leached phosphate throughout the testing period. Eighty percent of the sorption capacity of phosphate had been used when the cumulative loadings to the columns were greater than 0.2 mg-PO_4^{3-}/g zeolite, 0.5 mg-PO_4/g peat, 1.5 mg-PO_4^{3-}/g carbon, and 3 mg-PO_4^{3-}/g agrofiber. Sakadevan and Bavor, (1998) studied the phosphate adsorption characteristics of soil, slags and a clinoptilolite material (zeolite) to be used as substrates in constructed wetland systems and examined the potential to improve their adsorption characteristics. The experiment used Freundlich and Langmuir adsorption isotherms to describe the adsorption behaviors.

The principles of adsorption

In the fundamentals of adsorption, it is useful to distinguish between physical adsorption (physisorption) and chemical adsorption (chemisorption).

1. Physisorption

Physisorption involves the balancing of a weak attractive force, for example, of van der waals, between the surface and the adsorbate, with the repulsive force associated with close contact. The process is always exothermic and the energy given out on adsorption, the heat of adsorption,

ΔH_{ads}, is low, typically in the region -10 to -40 kJ mol^{-1} (McCash, 2001). Physisorption is non-specific and any atom or molecule can adsorb on any surface under appropriate experimental conditions; large amounts of physisorption are favored when the surface is at low temperature.

2. Chemisorption

Chemisorption is characterized mainly by a strong chemical bond forming between the surface and the adsorbate. Because chemisorption involves chemical bonding, also, it involves the exchange of electrons between the adsorbing molecule and surface. The heats of adsorption for chemisorption are generally larger than for physisorption. ΔH_{ads} tends to be in the range -40 to -1000 kJ mol^{-1} (McCash, 2001) and it is found that chemisorbed layers with large heats of adsorption tend to be very stable at high temperature. The bond formed may be ionic, covalent, or a mixture of the two.

The comparison of chemisorption and physisorption

A summary to compare the chemisorption and physisorption processes in order to help to distinguish between them follows in Table 5.

Table 5 Comparison of chemisorption and physisorption processes.

	Chemisorption	Physisorption
ΔH_{ads}	-40 to -1000 kJ mol^{-1}	-10 to -40 kJ mol^{-1}
kinetic of activation	can be activated	non-activated
number of layer	monolayer	multilayer
chemical reaction	can cause reactivity change in the adsorbate	little change
specificty	normally dependent on specific adsorbate surface interaction	non-specific, needs low temperature to get substantial amounts

Source: McCash (2001)

Energetic of adsorption

The thermodynamics of adsorption only enables one to obtain the magnitude of the bond strength in adsorption; one cannot also discover the nature of the forces involved in bonding. A number of quite different types of forces are responsible for the bonding which keeps the adsorbate and adsorbent together. The forces may be identified as:

1. Dispersion forces

Dispersion forces arise from fluctuations in the electron density clouds of two atoms. The time average of the charge distribution in these atoms may be symmetrical, yet the charge fluctuations are sufficient to induce resonance and cause an attraction. The resultant force has a relatively long range. Thus, they often account for the major part of the adsorbate-adsorbent potential. These forces exist in all types of matter and always act as an attractive force between adjacent atoms and molecules no matter how dissimilar.

2. The overlap or repulsive forces

When an adsorbate molecule comes very near to a solid surface molecule to allow interpenetration of the electron clouds, a repulsive interaction will arise and their electron orbitals or eigen functions overlap.

3. Dipole interaction

These forces arise in addition to the above forces whenever a non polar adsorbate is adsorbed on a polar adsorbent, or whenever a polar adsorbate is adsorbed on a non-polar or a polar adsorbent. In the latter instance, the action of the polar partner is also to induce an electric moment in the non-polar molecule.

4. Valency forces

Valency forces are similar to the repulsive forces in that they arise at sufficiently close distances. They arise owing to the electron orbitals overlapping in a suitable way and they are responsible for chemisorption.

5. Interaction forces

These are the forces between the atoms or molecules of the bound adsorbate themselves. These forces must be considered in both physisorption and chemisorption when the coverage of adsorbate on the adsorbent attains the stage at which the distance separating adsorbate molecules is small.

Adsorption equilibria

Adsorption from aqueous solution involves concentration of the solute on the solid surface. The term adsorption equilibrium is an equilibrium state in which equal amounts of solute eventually are being adsorbed and desorbed simultaneously; in other words, the rate of adsorption equals desorption. Therefore, at equilibrium, no change can be observed in the concentration of the solute on the solid surface or in the bulk solution.

Adsorption isotherm

Adsorption isotherm is the presentation of the amount of solute adsorbed per unit of adsorbent as a function of the equilibrium concentration in bulk solution at constant temperature. Measurements of isotherms can be made using either gravimetric or volumetric techniques. The shape of the adsorption gives qualitative information about the adsorption process and the extent of the surface coverage by the adsorbate. The five main shapes of adsorption isotherm are shown in Figure 2.

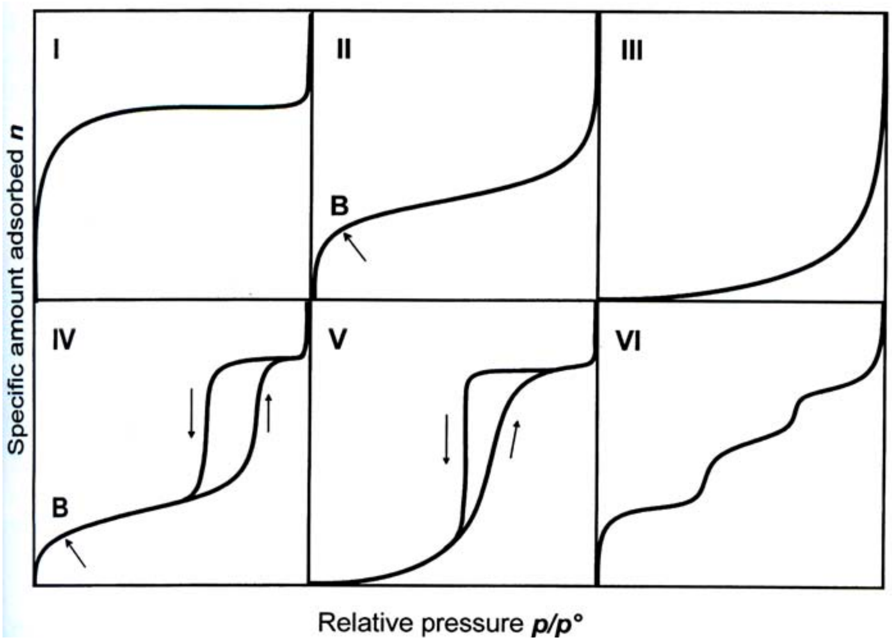


Figure 2 The five main shapes of adsorption isotherm, given as plats of coverage against equilibrium pressure.

Source: Elain M. McCash, 2001

The type I is associated with systems where adsorption does not proceed beyond the monomolecular layer. This isotherm describes ideal chemisorption, where molecules chemisorb unit the surface becomes saturated with adsorbate, whereupon adsorption ceases. The type II is a further increase in the amount adsorbed and many layers are ultimately adsorbed. This type is usually associated with physisorption. The other three types: the type III is associated with multilayer formation from the onset, and types IV and V are associated with formation of monolayer where there are variations of heat of adsorption with θ.

The Langmuir adsorption isotherm

This is the most commonly used model for an adsorption isotherm and describes ideal chemisorption systems. The assumptions made in this model, which is also called *the ideal localized monolayer*, is that:

1. Adsorption occurs on specific sites and all adsorption sites are identical.
2. Each site can accommodate only one molecule i.e. monolayer.
3. The energy for the adsorption is independent of how many of the surrounding sites are occupied and it is the same at all sites.
4. The adsorbed molecule cannot migrate across the surface or interact with adjacent molecules.

The Langmuir equation was originally derived from kinetic consideration.

$$\text{Rate of adsorption} = k_a P(1-\theta) \qquad \text{(eq.1)}$$

$$\text{Rate of desorption} = k_d \theta \qquad \text{(eq.2)}$$

Where θ = fraction of the site already filled

$(1-\theta)$ = fraction of the site to be vacant

k_a = rate of adsorption

k_d = rate of desorption from a fully covered surface

P = pressure

At equilibrium the amount of molecules in the adsorbed state is constant; thus:

$$k_a P(1-\theta) = k_d \theta \qquad \text{(eq.3)}$$

and

$$\frac{\theta}{(1-\theta)} = \frac{k_a}{k_d} p \qquad \text{(eq.4)}$$

Taking k_a/k_d = b, which is the adsorption equilibrium constant.

Therefore, Equation 4 becomes:

$$bP = \frac{\theta}{1-\theta} \qquad \text{(eq.5)}$$

or

$$\theta = \frac{bP}{1+bP} \qquad \text{(eq.6)}$$

This is known as the Langmuir adsorption isotherm. For adsorption from solution by solid adsorbents, the Langmuir adsorption isotherm is expressed as:

$$X = \frac{X_m b C_e}{1+bC_e} \qquad \text{(eq.7)}$$

Where $X = x/m$, which is the amount adsorbed per unit weight of
adsorbent (the same as Freundlich equation)
X_m = amount of solute adsorbed per unit weight of adsorbent
Required for monolayer coverage of the surface
i.e. monolayer capacity
C_e = equilibrium concentration of the solute
b = constant related to the heat of adsorption

For linearization of the data, Equation 7 can be written in the form

$$\frac{C_e}{X} = \frac{1}{bX_m} + \frac{C_e}{X_m} \qquad \text{(eq.8)}$$

Dividing Equation 8 by C_e:

$$\frac{1}{X} = \frac{1}{X_m} + \left(\frac{1}{C_e}\right)\left(\frac{1}{bX_m}\right) \qquad \text{(eq.9)}$$

Plotting $1/X$ against $1/C_e$ is straight-lined

$$\text{slope} = \frac{1}{bX_m}$$

$$\text{intercept} = \frac{1}{X_m}$$

The Langmuir isotherm can be determined the monolayer capacity (X_m), where X_m defines the total capacity of the adsorbent for a specific adsorbate.

The Freundlich adsorption isotherm

This form of isotherm was developed to take into account the observation of a coverage dependence of the heat of adsorption. For the Freundlich adsorption equation is perhaps the most widely used mathematical description of adsorption in aqueous systems. The assumptions made in the Freundlich isotherm are:

1. The heat of adsorption declines logarithmically with coverage so $\Delta H = -\Delta H_m \ln \theta$ (ΔH_m, the heat of adsorption for the monolayer, is a constant for a given system).

2. θ has values which do not approach 0 or 1, that is, it applies for intermediate coverage only, usually in the range 0.2-0.8.

3. This isotherm can be applied to both chemisorption and physisorption systems.

Empirically, the Freundlich equation is expressed as:

$$\frac{x}{m} = KC_e^{\frac{1}{n}} \qquad \text{(eq.10)}$$

Where x = amount of solute adsorbed
m = weight of adsorbent
C_e = solute equilibrium concentration
K and 1/n = constants characteristic of the system

For linearization of the data, it is written in logarithmic form

$$\log\frac{x}{m} = \log K + \frac{1}{n}\log C_e \qquad \text{(eq.11)}$$

Substituting $C_o - C_e$ in Equation 11 for x

$$\log\left(\frac{C_o - C_e}{m}\right) = \log K + \frac{1}{n}\log C_e \qquad \text{(eq.12)}$$

Where C_o = initial concentration

Plotting $\log(C_o - C_e)/m$ versus $\log C_e$ should give a straight line.

$$\text{slope} = \frac{1}{n}$$

$$\text{intercept} = \frac{1}{K}$$

The Brunauer-Emmett-Teller (BET) adsorption isotherm

The Langmuir isotherm is limited to the adsorption of one monolayer of adsorbate. The formation of multilayers is modeled by BET isotherm and this essentially uses the basis of the Langmuir model and extends it to encompass physisorbed multilayer. The assumptions made are that:

1. Each layer of adsorbate is treated as a Langmuir monolayer and each layer must be complete before the next layer starts to form.
2. The heat of adsorption for the first layer is characteristic of the adsorbate/adsorbent system.
3. The heat of adsorption for subsequent layers is equal to the heat of condensation.

The resulting equation for BET equilibrium isotherm is

$$V = \frac{V_m BP}{(P_o - P)[1 + (B - 1)P / P_o]} \qquad \text{(eq.13)}$$

Where V = volume of gas adsorbed at pressure
V_m = volume adsorbed at infinite pressure
P_o = saturation vapor pressure of the saturated liquid sorbate
B = constant

by

$$B = \frac{a_1 b_2}{a_2 b_1} e^{(E_1 - E_L)/RT} \qquad \text{(eq.14)}$$

which can be simplified to

$$B = e^{(E_1 - E_L)/RT} \qquad \text{(eq.15)}$$

Where a_1 and a_2 = rate of condensation on the first and second layers
b_1 and b_2 = rate of evaporation from first and second layers
E_1 = heat of adsorption at first layer
E_L = heat of liquefactions of the bulk phase
the term $E_1 - E_L$ is the net heat of adsorption.

For the adsorption from solution, the application of the BET equation takes the form

$$X = \frac{X_m BC}{(C_s - C_e)[1 + (B-1)C_e / C_s]} \qquad \text{(eq.16)}$$

Where C_s = solubility of the solute in water at a specified temperature.
Transforming Equation 16 to

$$\frac{C_e}{X(C_s - C_e)} = \frac{1}{X_m B} + \frac{(B-1)}{X_m B} \frac{C_e}{C_s} \qquad \text{(eq.17)}$$

plotting $\frac{C_e}{X(C_s - C_e)}$ versus $\frac{C_e}{C_s}$ should give a straight line

$$\text{slope} = \frac{(B-1)}{X_m B}$$

$$\text{intercept} = \frac{1}{X_m B}$$

Adsorption on surfaces can take place via three mechanisms illustrated in Figure 3:

1. The inner-sphere surface complex involves the cavity.
2. The outer-sphere surface complex includes the cation salvation shell.
3. The diffuse-ion swarm involves ions that are fully dissociated from surface functional groups and freeing to nearby in solution.

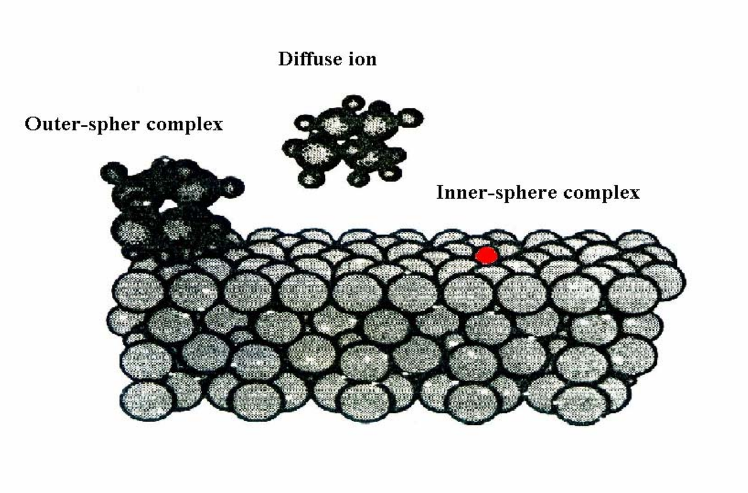
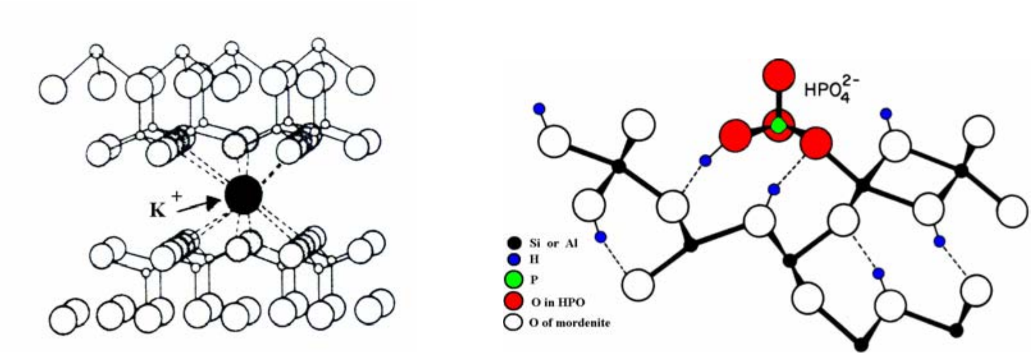


Figure 3 The three mechanism of ions adsorption on siloxane surface

Source: Sposito (1989)



(a) (b)

Figure 4 (a) inner-sphere surface complex of K^{2+} on mordenite

(b) inner-sphere surface complex of HPO_4^{2-} on mordenite

Source: Sposito (1989)

Surface charge

Zeolite surfaces develop electrical charge in two principal ways: either from isomorphic replacement among ions of different valence in zeolite, or from the reactions of surface functional groups with ions in solution (Sposito, 1989).

The net total particle charge, σ_P, is parameter depending on chemical conditions. It can represent by equation:

$$\sigma_P = \sigma_0 + \sigma_H + \sigma_{IS} + \sigma_{OS} \qquad \text{(eq.18)}$$

Where σ_0 = permanent structural charge

σ_H = net proton charge

σ_{IS} = inner-sphere complex charge

σ_{OS} = outer-sphere complex charge which

$$\sigma_H = q_H + q_{OH}$$

Where q_H and q_{OH} = mole of ion H^+ and OH^-

When the surface charge is non zero, σ_P must be balanced with the diffuse-ion swarm. This ions move about freely near enough to zeolite surface to create the effective surface charge, σ_D. The statement of the balance of surface charge represent by equation:

$$\sigma_P + \sigma_D = 0 \qquad \text{(eq.19)}$$

From this equation, points of zero charge are pH values at which one or more of surface charge components vanishes. Table 6 showed the most important points of zero charge.

Table 6 Some points of zero charge

Name	Symbol	Defining condition
Point of zero charge	PZC	$\sigma_P = 0$
Point of zero net proton charge	PZNPC	$\sigma_H = 0$
Point of zero net charge	PZNC	$\sigma_{IS} + \sigma_{OS} + \sigma_D = 0$

Source: Sposito (1989)

From Table 6, PZNC equals zero when the moles of adsorbed cation charge equals the moles of adsorbed anion charge, if cations and anions in surface complexes balance in charge, there will be no need for a diffuse ion swarm contribution ($\sigma_D = 0$), from equation 19, it made also $\sigma_P = 0$, thus PZNC equal PZC.

Iso-electric point (IEP) is parameter for characterizing surface properties of colloids. It is the pH at the net charge on the slip surface of the electric double layer is zero and so the potential equals zero. The relationship between the overall PZC of a mixture and the individual IEP of each component are eq.20.

$$PZC = \sum_i f_i IEP_i \qquad \text{(eq.20)}$$

Where f_i = the fraction of i component

IEP_i = the IEP of component i

Type of adsorption on the surface

Soil on earth may be classified into two basic categories: permanent charge soil and variable charge soil (Yu, 1997). The permanent charge soil is surface charges of layer silicate minerals. The variable charge soil is surface charges of free oxide, iron, aluminum, manganese oxide and humus. It is difficult to have a clear-cut definition between the two categories of soils.

The charges on surface can be positive or negative charges, thus the counter ions adsorbed on surface contain could be cation and anion. There are four types of adsorption force (Yu, 1997).

1. Electrostatic adsorption of cations

Electrostatic adsorption of cations is the adsorption of cations by particle which the interaction force between cations and the surface of particle during adsorption is electrostatic in nature. The heterogeneity in distribution of ions in soil colloidal systems is interpreted mainly in terms of electrostatic interactions occurring at the interface between soil colloidal particles and the liquid phase. When cations are electrostatically adsorbed by negatively charge soil, it can be expected that the affinity of soil colloid surface for cations of different valencies should generally be of the order $M^+ < M^{2+} < M^{3+}$.

2. Electrostatic adsorption of anions

Electrostatic adsorption of anions is the adsorption subject to attractive force of positive charges and repulsive force of negative charge carried by particle, and they stay in the outer layer of the electric double layer through dynamic balance between electrostatic attraction and thermal motion. Some anion species both electrostatic force and specific force may be involved during their interactions with variable charge soils.

3. Specific adsorption of cations

Specific adsorption of cations is the adsorption of cations by particle with specific forces between the surface of particle and cations. This adsorption is related to both the nature of cations and the surface properties. Most of cation species can be adsorbed specifically to the surface of soil. Examples belong to heavy metals, such as copper, zinc, and cobalt, belong to heavy metals. Alkali metal and alkaline earth metal ions can also be adsorbed specifically to some extent by soil under certain conditions. Nevertheless, specific adsorption is less importance when compared to electrostatic adsorption and the mechanism involved may be different from that for heavy metals. The reason of the difference in properties between the transition metal ions and alkali metal and alkaline earth metal ions with respect to adsorption lies primarily in the difference in their atomic structure. The transition metal ions are characterized by a large amount of electric charge in the atomic nucleus, small ionic size, and strong polarizability. By contrast, alkali metal and alkaline earth metal ions are characterized by a smaller amount of electric charge in the atomic nucleus, larger ionic size, and weak polarizability.

4. Coordination adsorption of anions

Coordination adsorption of anions is the specific adsorption of anions by particle. For anions, the mechanism of specific adsorption is ligand exchange between these ions and some groups that have already been coordinating linked on the surface of particles. For variable charge soil, phosphate is the strongest specifically adsorbed anion species. The valence status of phosphate ions is trend to change with the change in environmental conditions. Therefore, the phenomenon of phosphate adsorption is rather complex and it is often difficult to make definitive interpretations of experimental results. Al-OH, Fe-OH, Al-OH_2, and Fe-OH_2 groups on the surface of soil particles are the important sites for coordination adsorption of anions. Consequently, when a soil contains large amounts of aluminum and iron oxides, the phenomenon of coordination adsorption of anions will be more pronounced.

Zeta potential

Zeta potential (ζ) can be defined as the potential at the surface of shear. It is probably fairly close to the stern potential in magnitude, and definitely less than the potential at the surface (Hiemenz and Rajagopalan, 1997). The relative values of these different potentials are shown in Figure 5. Distances within the double layer are considered large or small, depending on their magnitude relative κ^{-1}. Thus in dilute electrolyte solutions, in which κ^{-1} is large, the surface of shear- which is close to the particle surface even in absolute units- may be safely regarded as coinciding with the surface in units relative to the double layer thickness.

Stern is to divide the aqueous part of the double layer by the hypothetical boundary known as the *stern surface* or stern plane (Hiemenz and Rajagopalan, 1997). The stern surface is situated a distance (δ) from the actual surface. The stern surface is drawn through the ions that are assumed to be adsorbed on the charge wall.

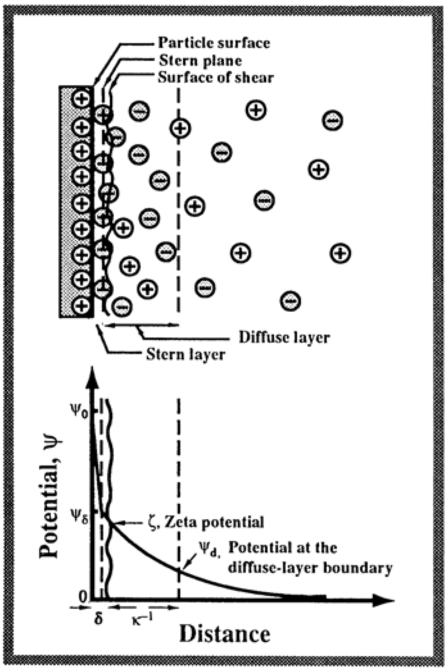


Figure 5 The variation of potential with distance from a charged wall in the presence of a Stern layer

Source: Hiemenz and Rajagopalan (1997)

Effect of temperature on amount adsorbed

The effect of temperature on the amount of material chemisorbed at equilibrium varies in a complex way with different systems. For gas system, the amount is usually correlated with the relative pressure. At lower temperature, the amount observed to be chemisorbed is frequently less than this because the rate of adsorption is so low that saturation is not reached.

Effect of time on amount adsorbed

In general, when the time of adsorption increasing amount of adsorbed is also increasing until the adsorption achieve equilibrium. At equilibrium, the rate of adsorption equal the rate of desorption lead into the maximum of adsorbed on adsorbent. The time after equilibrium, amount of adsorbed is decreasing because the rate of desorption more than the rate of adsorption.

Zeolites are the most materials use in industry. There was used to pollutants removal, catalyst including the reactants for various reactions.

Definition of Zeolite

Zeolites are mainly compounds of crystalline, naturally-occurring aluminosilicate minerals. They have a three-dimensional framework structure bearing $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ coordination polyhedra linked by all their corners. Their frameworks generally are very open and contain channels and cavities in which are located water molecules and cations. Water molecules are readily lost and regained when the zeolites are heated and cations often have a high degree of mobility giving rise to easy ion exchange. In their channels and cavities they are able to selectively take up some molecules into porous structure.

There are 39 kinds of natural zeolites and about 100 kinds of synthesized zeolites (Dyer, 1998). Natural zeolites are formed by hydrothermal transformation of basalt, volcanic ash, and pumice which can be found e.g. in basalt cavities and in large sedimentary deposits. The most important industrial natural zeolites are clinoptilolite, mordenite, chabazite, and erionite. Synthesized zeolites are synthesis of crystalline from an inhomogeneous gel, created from a silica sources and an alumina sources, combined with water under high pH conditions generated by hydroxyl ion concentrations. Control of the SiO_2:Al_2O_3 ratio in this gel qualifies the final framework composition of the product taken into the zeolite composition

Structure of zeolites

Zeolites have framework structures constructed by joining $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ coordination polyhedra. These tetrahedra are assembled together so that the oxygen at each corner is shared with an identical tetrahedron, Si or Al, as shown in Figure 6.

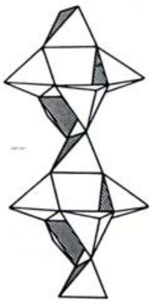


Figure 6 The tetrahedra linked together to create a three-dimensional structure Source: Dyer (1988)

Composition of zeolite consist of Si, Al, and O positions in space relative to each other and excluding cations and water molecules sited within cavities and channels of framework.

Zeolites are a porous solid and as promoters in liquid-phase organic reactions provide some advantages:

1. Easy to separate products from solids by means of a sample procedure of filtration.
2. Adsorption or inclusion of reagent molecules into the small pores of solids with nanometer dimensions organizes the molecules in close proximity to lower the activation entropy of reaction.
3. The coexisting acid and base sites on solid surfaces accelerate organic reactions.
4. Pore structures of the solid discriminate between reactant molecules with respect to molecular dimensions.

Natural zeolite

In nature, the zeolites are often formed where volcanic rock of specific chemical composition is immersed in water so as to leach away some of the components. The composition and pore size depend upon what kinds of rock minerals are involved.

Mordenite is a kind of natural zeolite. Their structure type is MOR and based upon the 5-1 units in SBU’s. The 5-1 units are linked into a series of chains joined together to form major channels, one restricted by 12 oxygen windows and one by 8 oxygen windows.

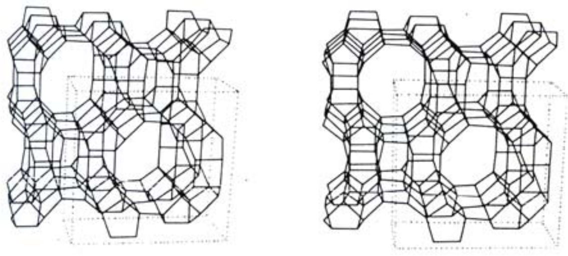


Figure 7 The structure of mordenite
Source: Dyer (1988)

Mordenite is found widespread in industrial applications as highly selective adsorbents, ion exchangers and, most importantly, catalysts of exceptionally high activity and selectivity in a wide range of reactions. Hayakawa *et al.* (1996) studied adsorption of cationic surfactants on mordenites. This study found adsorption isotherms of dodecyltrimethylammonium bromide (DTAB) and decyltrimethylammonium bromide (DeTAB) on mordenites were dependent on Si/Al ratios. DTAB showed a stronger adsorption than DeTAB did and both surfactants interacted more strongly with mordenites of higher Si/Al ratio. The data was ascribed to the increasing hydrophobic interaction between surfactant and mordenite with increasing Si/Al ratio. Deka and Vetrivel (1998) studied the adsorption and diffusion behavior of large molecules inside the micropores of zeolites such as faujasite, zeolite L, mazzite, and mordenite. They used the efficiency of force field energy minimization technique to investigate them. The results indicated that mordenite is a good catalyst for selective synthesis of *p*-isobutylethylbenzene. The adsorptions of the molecules in general are energetically favorable when the alkyl groups have maximum interaction with the surface of the zeolite pores. Poborcbiia *et al.* (1998) used Raman and X-ray absorption spectroscopy to study influence of ion exchange and method of selenium incorporation into mordenite channels on the structure of incorporated selenium species. The results showed that Se chains prepared by Se vapor adsorption are more regular than Se chains prepared by pressure injection of liquid Se. Selenium incorporated into II-form of mordenite was found to be located not only in the original mordenite channels, but also in meso-channels organized due to partial destruction of the interchannel walls. Ahmad *et al.* (1998) used FTIR spectroscopy to study acetophenone adsorption on mordenite and acid-leached mordenite. Moreover, the experiment studied the effects of dealumination characterized by pyridine adsorption and ^{29}Si and ^{27}Al magic angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR). The results showed acetophenone adsorption on mordenite with weak physisorption that was accompanied by three other modes of adsorption involving hydrogen bonding to internal and external silanol groups, hydrogen bonding to Brønsted acidic Si(OH)Al groups, and ligation to Lewis acidic Al^{3+} ions. Dealumination of mordenite by acid leaching converted a proportion of the Si(1Al) species to Si(OAl), reduced the concentrations of framework and extraframework Al and of Si(OH)Al groups, greatly reduced the population of Lewis acidic sites, and generated additional silanol groups. Moreau *et al.* (2002) studied the influence of Na exchange on the acidic and catalytic properties of an HMOR zeolite. The experiment used IR spectroscopy to characterize the hydroxyl groups of a series of NaHMOR samples resulting from sodium exchange of an HMOR sample. From the experiment, they found Na exchange occurs preferentially with the OH groups of the side pockets and the first Na cations exchange causes a significant decrease in the activity of mordenite and decrease in the turnover frequency of the protonic sites. In addition, when the selectivities are compared at the same temperature, sodium exchange of mordenite causes an increase in the isomerization selectivity. Metaxas *et al.* (2003) used mordenite and other adsorbents to remove thorium. The results showed that mordenite (NaMOR) utilized 38.6% of the theoretical ion-exchange capacity based on Al content. Wernert *et al.* (2005) studied methods of elimination of uremic toxins such as urea, uric acid, creatinine, p-cresol and indoxyl sulfate from solutions by adsorption onto zeolites. They studied the physical and chemical properties of microporous materials varied following pore size, acidity, hydrophobicity, grain size, charge compensating cations, and stabilization by high pressure hydrothermal treatment. The results showed for initial concentrations close to that of persons having renal failure, it is possible to eliminate 75% creatinine by adsorption onto an acidic mordenite. In wastewater treatment, natural zeolite(clinoptilolite and mordenite) supplied from Dogantepe (Amasya) region in Turkey was used to remove ammonium ion from municipal wastewater (Sarioglu, 2005). The highest adsorption capacity obtained with acid-washed sample was determined to be 1.32 mg NH_4^+-N/g and the cation exchange capacity of Dogantepe zeolite was found to be 164.62 meq. per 100 g. However, the efficiency of the natural or acid washed zeolite can be further increased through conditioning with Na.

Researchers have studied the structure of mordenite. Korkuna *et al.* (2005) characterized mordenite using adsorption, AFM, FTIR, and TG–DTA methods. The initial natural mordenite have small specific surface area which increases significantly after their modification. The results of TG data show the presence of several types of water, and larger amounts of water desorbed from H-forms of mordenite up to 120ºC that can be caused by stronger changes in the mordenite structure. Covarrubias *et al.* (2005) synthesized zeolites with high Cr(III) exchange capacity (CrEC) using kaolin and natural mordenite as starting materials, and evaluated the effect related to the reaction time on the crystallization/transformation process and on product CrEC. The XRD, FTIR, SEM, N2-adsorption and TG/DTG were used to characterize the synthetic material. Synthesized zeolite products presented higher Cr(III) exchange capacity than commercial zeolites. These results suggest that the use of these synthesized materials in Cr(III) removal from industrial wastewater could be promising.

Moreover, other natural zeolites, clinoptilolite, perlite, and diatomite were also used as adsorbent ion exchangers to eliminate contaminant ions from wastewater. Doula *et al.* (2002) used clinoptilolite to adsorb copper ion. Copper adsorption was found to increase with increased pH and with decreased electrolyte concentration. Besides, they also examined effects of [HC] differentiation on Cu adsorption and on Al/Si dissolution by FTIR. From the study of FTIR, it was proposed that the Cu species caused the destruction of H-bonded structures, whereas K adsorbed species were located at exchangeable sites after an ion-exchange process between K and Ca, Mg, and Na from the zeolite's surface. Armağan *et al.* (2004) studied equilibrium of reactive azo dyes, color from textile effluents, adsorbed into clinoptilolite. They used a series of batch adsorption experiments to investigate the adsorption & reactive dyes into clinoptilolite. The adsorption results indicated that natural zeolite has a limited adsorption capacity for reactive dyes but can be distinctly improved by modifying its surfaces with quaternary amines with natural clinoptilolite comparison with a modified clinoptilolite for the adsorption densities of dyes, natural clinoptilolite yielded negative or slightly positive values, while those with modified clinoptilolite gave adsorption densities in the range of 2.9 to 7.6 mg/g. Englert and Rubio (2005) studied ammonia removal from aqueous solutions using a natural Chilean zeolite. The zeolitic-rich tuff sample was mainly composed of clinoptilolite and mordenite. Kinetics of ammonia removal appeared to proceed through ion-exchange and was rapid at neutral pH value, with removal capacities up to 0.68 meq NH^{4+}/ g. The excellent equilibrium data fitting by Langmuir isotherm model. The results indicate a significant potential for the Chilean natural zeolite as an adsorbent/ion-exchange material for wastewater treatment and water reuse applications.

Perlite is defined as a naturally occurring glassy volcanic siliceous rock which is inexpensive and easily available in Lopburi Province of Thailand and elsewhere around the world. Consequently, the scientist was attention to used perlite as materials for eliminate contaminants in wastewater. Mathialagan and Viraraghavan (2002) used perlite for removal of cadmium from aqueous solutions. The results found optimum pH for adsorption to be 6.0, the rate of cadmium adsorption by perlite was rapid in the first hour of the reaction time and cadmium concentration reached equilibrium in 6 h. The maximum removal of cadmium obtained from batch studies was 55% as well as using Freundlich isotherm model to define adsorption equilibrium. Koumanova and Peeva-Antova (2002) studied the adsorption of *p*-chlorophenol (*p*-CP) from aqueous solutions on bentonite and perlite. The results found rapid adsorption 20–30 min after the beginning for every experiment. After that, the concentration of *p*-CP in the liquid phase remained constant. The adsorption equilibrium of *p*-CP on bentonite and perlite was described by the Langmuir and the Freundlich models. A higher adsorption capacity was observed for bentonite (10.63 mg g^{-1}) compared to that for perlite (5.84 mg g^{-1}).

Diatomite is a siliceous rock made up largely from the skeletons of aquatic plants called diatoms that is found in Lampang province. The usefulness of diatomite is the same as perlite. Akyüz *et al.* (2001) used natural diatomite from Kutahya-Alayunt (Anatolia, Turkey) adsorbed benzidine (bnz), 2,2′-bipyridyl (2,2′-bpy) and 4-4′-bipyridyl (4-4′-bpy). They used FTIR to investigate the nature of the surface species formed on diatomite after sorption. The vibrational results indicated the presence of chemisorbed species but no physical sorbed species were detected. Summarization of this research indicated that most of the adsorbed 2,2′-bpy molecules coordinated to surface cations through ring nitrogens as bidentate ligands and some of the adsorbed 2,2′-bpy molecules formed anionic surface species. In this case, adsorbed 4,4′-bpy do not observe anionic surface species. The results showed that natural diatomite can be an adsorbent.

Water contamination resulting from dyeing and finishing in textile industry is a major concern. Discharging large amount of dyes in water resources accompanied with organics, bleaches, and salts can affect the physical and chemical properties of freshwater. If dyes are released into water it leads to water pollution. Therefore, researchers have tried to remove them from water. Erdem *et al.* (2005) studied adsorption of some textile dyes by diatomite. The study used batch adsorption techniques at 30ºC to adsorb these textile dyes onto diatomite earth samples. The adsorption behavior of textile dyes on diatomite samples was investigated using a UV–vis spectrophotometric technique. The experiment investigated the effect of particle size of diatomite, diatomite concentration, the effect of initial dye concentrations, and shaking time on adsorption. Adsorption coverage over the surface of diatomite was studied using two well-known isotherm models: Langmuir's and Freundlich's. These results suggest that the dye uptake process mediated by diatomite has potential for large-scale treatment of textile mill discharges. Values of the removal efficiency of the dyes ranged from 28.60 to 99.23%. The results showed that natural diatomite holds great potential to remove textile dyes from wastewater. Khraisheh *et al.* (2004) studied the effect of OH and silanol groups in the removal of methylene blue, reactive black (C-NN), and reactive yellow (MI-2RN) from aqueous solution by calcined and raw diatomite at 980ºC. This study demonstrated the importance of the various functional groups on the mechanism of adsorption and also studied the role of pore size distribution in the dye adsorption. The results revealed that the removal of hydroxyl groups from the surface of diatomite leads to a decrease in the adsorption. Shawabkeh and Tutunji (2003) used diatomaceous earth (diatomite) to adsorb the basic dye, methylene blue, from an aqueous solution. This study investigated the effect of initial dye concentrations, adsorbent particle size and concentration, and agitation speed on adsorption and adsorption isotherms obtained at different solution temperatures, which revealed an irreversible adsorption with a capacity of 42 mmol dye/100 g diatomite reached within 10 min. This value slightly increases with increasing the solution temperature. From the results there was a better fit to the experimental data than that of Langmuir's and Freundlich's. It was found that the kinetics of adsorption of methylene blue onto the surface of diatomite at different operating conditions is best described by the pseudofirst-order model.

Additionally, natural zeolites are used in other applications such as gas separation, to improve catalysts, and also as a catalyst. Ackley *et al.* (2002) used natural zeolites including clinoptilolite, chabazite, mordenite, erionite, ferrierite and phillipsite, for gas separation. The results of the study indicated that these natural zeolites are particularly well suited for trace-gas removal.

In general, although natural zeolites are abundant and inexpensive, these attributes may not offset the effects of impurities and inconsistency of properties that have low efficiency to adsorb other ions relative to the more uniform synthetic zeolites. Therefore, researchers have tried to improve materials to have higher efficiency than from nature. Modification of the adsorptive properties of natural zeolites by ionexchange, thermal treatment and structural changes to improve adsorption is interesting to study. Silva *et al.* (1996) used ammonium hexafluorosilicate treating NH_4MOR for dealumination. The experiment studied the influence of the treatment on the physicochemical characteristics and catalytic properties. The results showed a decrease in the adsorption rate and capacity for organic molecules and in activity and stability for m-xylene transformation. Vergani *et al.* (1997) studied modification of mordenite catalysts for isopropylation of biphenyl in continuous flow reactors. They used the combinations of acid extraction and calcinations to modify it. The results showed the best highly crystalline modified mordenite had a low sodium content, a Si/A1 ratio of about 70, a secondary pore volume in mesopores of about 0.15 ml/g and a surface area in mesopores of about 30 m2/g. Lee and Ha (1998) modified mordenites by dealumination with HCl/steam or HF treatment. For this study in HCl/steam-treated mordenites, the framework aluminum was mainly removed, while in HF-treated mordenites, the framework silicon and aluminum were simultaneously removed. HCl/steam-treated mordenites had lattice parameters smaller than on HF-treated mordenites at the same SiO_2/Al_2O_3 weight ratios. Also, HCl/steam-treated mordenites had a higher proportion of strong acidsites than HF-treated mordenites. The mordenites treated by HCl/steam and HF formed secondary mesopores of 3.7 nm in diameter. Kosanovic *et al.* (1998) used high-energy ball milling (mechanochemical amorphization) in order to investigate the processes of transformation of different types of zeolites, A, X, and synthetic mordenite. The formation of an amorphous aluminosilicate initially, followed by recrystallization of mordenite during prolonged heating, is performed by heating ammonium-exchanged synthetic mordenite. The amorphous precursor obtained by ball milling of the ammonium-exchanged synthetic mordenite remains amorphous during heating at 1000ºC. Müller *et al.* (2000) used thermal treatment, leaching with oxalic acid, and treatment with $SiCl_4$ for dealumination of zeolites beta, mordenite, ZSM-5, and ferrierite. The results showed that dealumination of mordenite is thought to occur during the calcinations; it very easily dealuminated. Hernández-Guevara *et al.* (2000) used photoacoustic techniques and X-ray diffraction to study ternary compounds $Zn_xCd_{1-x}S$ ($0 \leq X \leq 1$) embedded in mordenite zeolite host. From the results, they found the thermal diffusivity, thermal effusivity and band-gap as functions of the X parameter. Mohamed (2002) studied the effect of acid dealmination of the Na–mordenite zeolite on the dispersion of added Mo. As a result, Mo/zeolite catalysts have been extensively employed in the petroleum industry for their valuable activities, e.g., hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions. The results of obtained Mo-dealuminated mordenites showed higher surface areas than those of Mo-free ones. The affinity of Mo encapsulated in dealuminated mordenites to water adsorption reflected varying interactions of water with Mo. Mohamed (2003) used Fe ion-exchanged mordenite catalyst for ethanol transformation. Park *et al.* (2003) studied occlusion of mordenite by non-nitrate salts such as $KClO_3$ and KH_2PO_4. The results demonstrated that KH_2PO_4 occluded mordenite about 2.1 % (w/w). This shows clearly that the occlusions of a variety of salts including non-nitrate salts could lead to further expansion of zeolite potential for salt occlusion. Chumbhalel *et al.* (2004) studied catalytic degradation of expandable polystyrene waste (EPSW) using mordenite and modified mordenites. They used hydrochloric acid treated mordenites at 98ºC and dried at 120ºC for 12 h. The results obtained H-mordenite zeolites with higher SiO_2/Al_2O_3 ratios. It is clear that dealumination by acid leaching of synthetic mordenite increases silica-to-alumina ratio without loss of framework structure and it reduces both weak and strong acid sites.

Because of the chemical components of mordenite have metals such as Fe, Ca, Na, and Mg (Manouchehri *et al.*, 2006) so the scientists were interesting to study effect of these metals involved adsorption on material surface and to extraction it from material for increase efficiency of material. Tuccillo *et al.* (1999) used hydrochloric acid 0.5 M to extract Fe from sediment. The results shown hydrochloric acid can dissolved poorly Fe oxide and small amounts of Fe in crystalline Fe oxide. Manouchehri *et al.* (2006) used ethylene diaminetetraacetic acid (EDTA) to extract trace and major elements such as Pb, Cu, Cd, Al, Ca, Mg, and Fe from soil. They used concentrations of EDTA varied from 0.002 to 0.05M. They used frame atomic adsorption spectrometry (FAAS) determined amount of cations concentration. At 0.05M concentration represents the excess of the reagent with respect to all extractable cations.

Zeolite as ion exchange

The advantage of zeolite as a promoter is that its acid and base properties can be modified through a simple procedure of ion exchange. The replacement of cations holds in their aluminosilicate anion framework by ions present in external solutions. Certain parameters control ion exchange properties of zeolite, i.e.:

1. The nature of both the competing ions with respect to their sizes and states of salvation inside and outside the zeolite.
2. The charge on zeolite framework coupled with framework geometry.
3. The temperature at exchange and the accessibility of sites can improve exchange kinetic.

4. The concentration of the external solution coupled with the presence or absence of ligands other than water molecules.

Zeolite as molecular sieves

When the zeolites are heated, the water is also removed and the voids created within the framework can take in other molecules. This process is called 'sorption' and the zeolites are said to 'sorb' molecules into their void volume, in other words, they act as 'sorbents'. That is to say, the sorbing molecules are described as 'guests' within the zeolite 'host'. From their geometry comes the ability of zeolites to separate mixtures of molecules on the basis of their effective sizes.

The stabilities of zeolite structures

1. Thermal stability

The commonly observed transformation of the zeolite structure is that promoted by water loss. This can cause a change from one zeolite structure to another, structure collapse to an amorphous phase or recrystallization to non-zeolitic materials. The critical water losses can occur over a wide temperature range.

2. Hydrothermal stability

The zeolites are formed in nature when they are exposed to water vapour at increased temperatures and/or pressures. Study of hydrothermal stability is of great importance to the regeneration processes used in association with the use of synthetic zeolites as catalysts, molecular sieves and dying agents.

3. Stability to acid

The reaction of zeolites with moderate acid molarities demonstrates that the first stage is a cation exchange whereby hydronium ion replaces the indigenous cations. It can be carried out even in zeolite able to link-to the hydrolysis phenomenon. If the zeolites are heated, water is lost and they form hydrogen zeolite, which are stable and are desirable catalysts.

4. Stability to alkali

The hydroxyl species in solution is a critical factor in some zeolite transformations. The pH of the gel precursor in syntheses determines products and so it is to be expected that alkaline treatment of existing crystalline zeolites might create structure changes.

5. Stability to ionizing radiation

Zeolite structures have demonstrated to be remarkably resistant to radiation and prolonged exposure to high neutron and gramma rays produces a negligible effect on the zeolite matrix. High beta ray is equally ineffectual. Clearly, these are the properties needed for the use of zeolites to treat aqueous nuclear waste.