CHAPTER II

BLACKGROUNDS AND LITERATURE REVIEW

2.1 Chromium

Chromium is a naturally occurring element found in animals, rocks, plants, soil, and in volcanic dust and gases. Chromium is present in the environment in several different forms. The most common forms are chromium (0), Chromium(III), and chromium(IV) (Table 2.1). All of chromium does not have taste or odor. Chromium(III) occurs naturally in the environment and is an essential nutrient. Chromium(IV) and chromium(0) are generally produced by industrial process. The metal chromium which is the chromium(0) form, is used for making steel. Chromium(VI) and chromium(III) are used for chrome plating, dyes and pigments, leather tanning, and wood preserving. The toxicity of chromium; breathing high levels of chromium(VI) can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death. Skin contact with certain chromium(VI) compounds can cause skin ulcers. Allergic reactions consisting of severe redness and swelling of the skin have been noted. Then, many federals of many country realize to the hazardous of chromium for example EPA has set a limit of 100 μg chromium(III) and chromium(VI) per liter of drinking water (100 μg/L). The occupational Safety and Health Administrator (OSHA) has set limit of 500 μg water soluble chromium III) compound per cubic meter of workplace air (500 $\mu g/m^3$), 1,000 $\mu g/m^3$ for metallic chromium(0) and insoluble chromium compounds, and 52 $\mu g/m^3$ for chromium(VI) compound for 8-houes work shift and 40-hours work weeks (Benoit, 1986)

Generally, the form of chromium (VI) in the solution is CrO_4^{2-} or $HCrO_4^-$ These forms depend on pH value and the concentration of chromium solution (Figure 2.1).

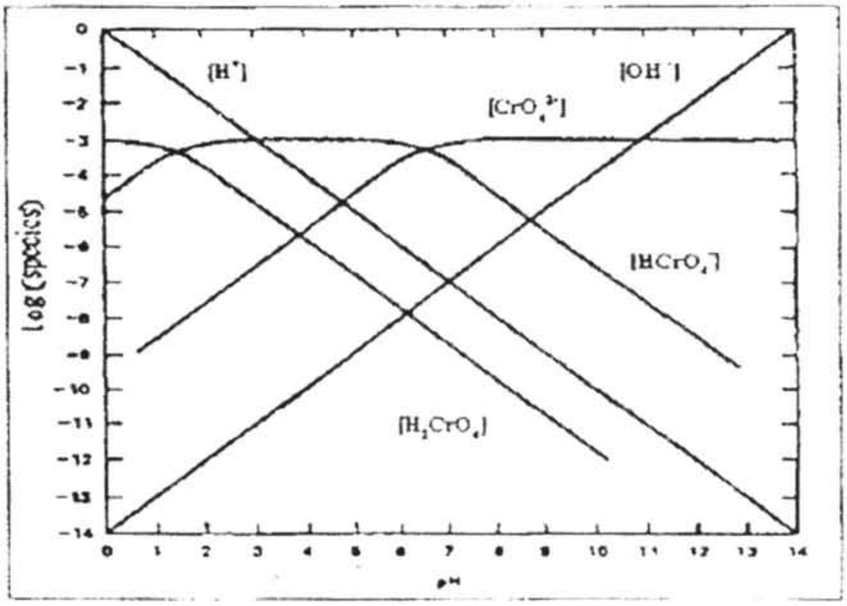


Figure 2.1 Scattered chromium in carried pH solution (Ku and Jung, 2001)

Table 2.1 Properties of chromium in wastewater (Rai et al., 1987)

Oxidation State	Oxide	Cation	Anion	Characteristics
6	CrO_3	-	CrO_4^{2-}(chromate) Cr_2O_7(dichromate)	Oxide acidic Anion stable
3	Cr_2O_3	Cr^{3+}(hydrated)	$[Cr(OH)]^{3-}$ (Chromate)	Oxide amphoteric Cation stable
2	(CrO)	Cr^{2+}(hydrated)	-	Oxide basic, Cation easily oxidized

2.2 Photocatalytic reaction

Photocatalytic process is applied in a large variety of reactions, For instance, total oxidations, dehydrogenation, hydrogen transfer, deuterium-alkane isotopic exchange, metal deposition, water detoxification, and gaseous pollutant removal (Hermann et al., 1999). In the two latter points, it can be considered as one of the new "advanced oxidation technologies" (AOT) for air and water purification treatment. Photocatalytsis can be defined as "a catalytic reaction involving light absorption by a catalyst or a substance"; and a "Catalyst" (CdS, TiO_2, ZnO, WO_3 and etc.) is a substance that increase the rate of reaction without modifying the overall standard Gibbs energy change in the reaction" (Hermann, 1999). The basic principles of photocatalytic process are the adsorption of substrates on catalytic surface and the irradiation process.

2.2.1 Adsorption process

The adsorption process consists of physical force (Van der Waal's force and electrostatic force) and chemical.

The Vander Waal's force is the attraction of free atoms or the neutral molecules. This phenomenon can appear cause of free driving of electron effect to the density of electron in atoms or molecules are not stable and these promote the polar atom or molecule. Thus, adsorption is able to appear. Vander Waal's Force has low efficiency for regeneration of the adsorbent. In addition, adsorption process contained by the catalyst for adsorb another molecule is adsorbent and another molecule that adsorbed is adorbate. The adsorption process is caused by London dispersion force, a type of Vander Waal's Force which exists between molecules. The force acts in a similar way to gravitational forces between planets. London dispersion force are extremely short ranged and therefore sensitive to the distance between then adsorbent surface and the adsorbate molecule.

The electrostatic force is the attraction of the polar molecule between the polar-polar or non-polar – non-polar molecule. Moreover, this force consist of many attraction characters for example; orientation effect, dispersion effect, induction effect.

The chemical forced occur when the adsorbent react with adsorbate to produce new chemical compound such as the adsorption between functional group and transitional metal at the surface of the adsorbent by used electron together, barter electron or donated electron. Then, the attraction between the adsorbent's ion and the adsorbete's functional force will occur. This force is the irreversible.

2.2.2 Irradiation process

The irradiation in the photocatalytic process uses ultraviolet light (UV) as a source of light for irradiation on the catalyst surface. Generally catalyst widely used in photcatalysis is semiconductors which have two band structures; the valance band, the high electric powers, and the conduction band which does not have electric powers. See figure 2.2 below, when irradiated catalysts the electron transfer from valance band to conduction band. This can promote catalyst to have high productivity of electron donor or electron accepter with another ion in the solution.

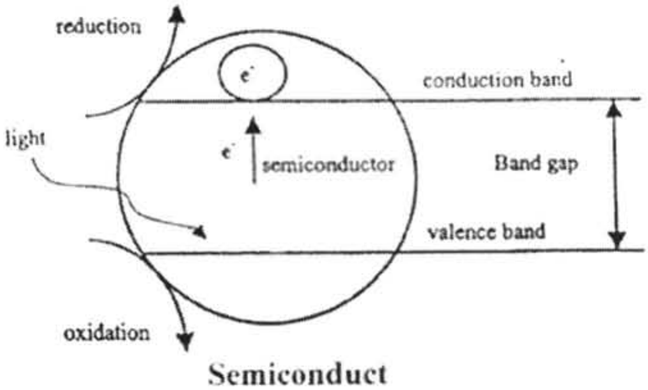


Figure 2.2 Reaction when irradiated catalysts (Fujishima, 1999)

The band gap between valance band and conduction band is specially for each catalyst as showed in figure 2.3. The band gap is the important in choosing the catalyst in photo reaction. Catalyst which has small band gap will not stable, electron from valence band can jump to conduction band and the recombination can occur. Other way, catalyst which has large band gap needs more energy for photocatalysis process.

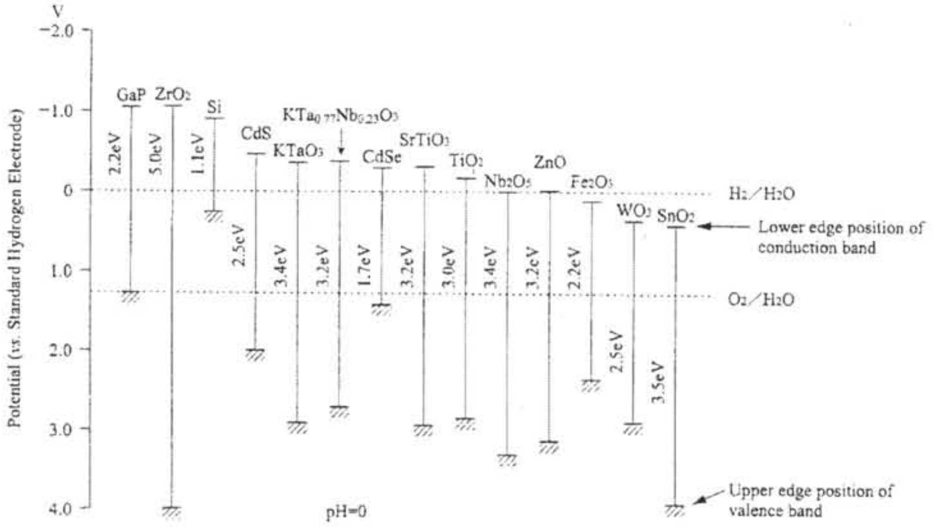
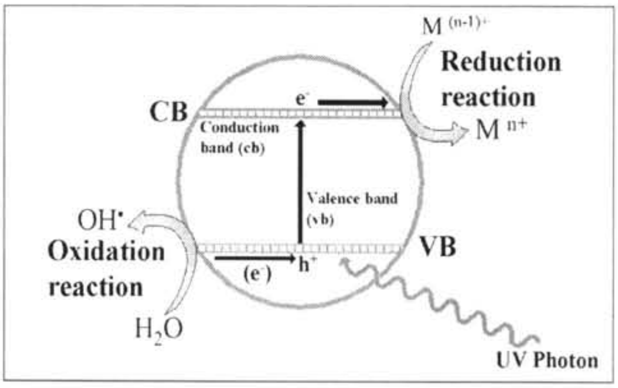


Figure 2.3 Band gap for each catalyst (Fujishima, 1999)

The qualification of TiO_2 is a neutral polar, when do not have excited state. The polar of TiO_2 depends on the environmental. For example, TiO_2 in the low pH solution (acidic solution) presents in positive polar. In contrast, TiO_2 in the high solution (basic solution) presents in negative polar. From this characteristics, TiO_2 is an alternative way for wastewater treatment especially in heavy metal and organic pollutant based on the redox reaction of photocatalytic process.

Photocatalytic process is well establish by the irradiation of TiO_2 with light energy greater than the band gap energy of the semiconductor ($hv > Rg = 3.2$ eV), conduction band electron (e^-) and valence band holes (h^+) are generated. After this primary event, part of photogenerated carriers recombine in the bulk of the semiconductor with heat emission, while the rest research the surface where the holes as well as the electrons act as powerful oxidants and reductants respectively. The photogenerated electron react with the adsorbed molecules O_2 on the Ti (IV)-sites reducing it to superoxide radical anion $O_2^{\bullet -}$, while the photogenerated holes can oxidize either the pollute molecules directly or the OH^- ions and the H_2O molecules adsorbed at the TiO_2 surface to $OH^{\bullet}$ radicals (Figure 2.4 (a)). These together with other highly oxidant species (peroxide radicals) are responsible for the primary oxidizing step in photocatalysis (Pelizzetti and Minero., 1993). According to this, the relevant steps of the photodegradation process at the semiconductor surface can be summarize by the reaction in figure 2.4 (b). The $OH^{\bullet}$ radicals formed on the illuminated semiconductor surface are very strong oxidizing agents with an oxidation potential of 2.8 V. These can easily attack the adsorbed pollute molecules or those located close to the surface of the catalyt, thus finally leading to their complete mineralization. (Poulios et al., 1999)



$TiO_2 + hv \longrightarrow e^- + h^+$

$M^{n+} + e^- \longrightarrow M^{(n-1)+}$

$Ti(IV) + OH + h^+ \longrightarrow Ti(IV)OH^{\bullet}$

$Ti(IV) + H_2O + h^+ \longrightarrow Ti(IV)OH^{\bullet} + H^+$

$R + h^+ \longrightarrow R$ (oxidized)

(a) (b)

Figure 2.4 (a) The TiO_2/solution interface under UV-illumination (Modifiled from Linsebigler et. al., 1995 and Hermann, 1999)
(b) Reaction on the TiO_2 surface under UV-illumination (Poulios et al., 1999)

2.3 Titaniumdioxide (TiO_2)

Titanium is common constituent of minerals, occurring in igneous rocks e.g., $BaTiO_3$, in silicates and iron-titanium oxides. Titanium dioxide (TiO_2) has been widely used in industry during the four last decades. The vast majority of traditional applications exploit its vary large dielectric constant and refractive index.

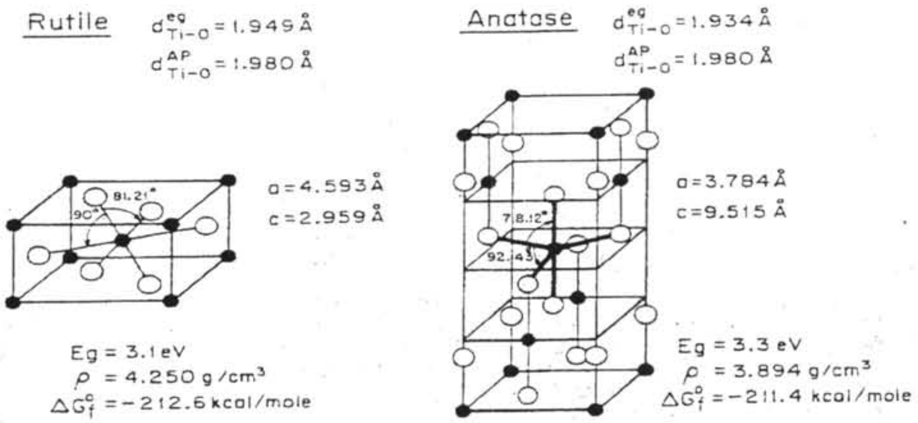


Figure 2.5 Convention primitive cells of rutile and anataste. Black and white spheres represent titanium and oxygen atom, respectively (Linsebigler et al., 1995

Table 2.2 Properties of rutile and anatase ((Fujishima et al., 1999)

Property	Rutile	Anatase
Crystalline form	Orthorhombic	Orthorhombic
Band gab energy(eV)	3.030	3.200
Hardness(Mohs)	6.0-7.0	5.5-6.0
Density(g/cm^3)	4.250	3.894
Gibbs free energy, $\Delta G_f°$	-212.6	-211.4
(kcal/mole)	4.593	3.784
Lattice constant, a (A°)	2.959	9.515
Lattice constant, c (A°)	1858 °C	Changes to rutile at
Melting point		high temperature
		~ 800°C

TiO_2 is a catalyst which has been extensively studied due to its photocatalytic activity under UV radiation, moreover its high surface activity, insoluble in diluted acid, non – toxicity, nature friendly and corrosion stability. Under favorable conditions, a wide range of organic and inorganic compounds can be mineralized to mineral acids, carbon dioxide and water or transformed into harmless species. TiO_2 appears in nature in three crystalline modifications, rutile (tetragonal), anatase (body center tetragonal) (Figure 2.5) and brookite (orthorhombic). Specifically in the anatase form promotes high activity in the photocatalyst. Upon increasing temperature, anatase is predominant, whereas if temperature reaches higher than 900°C anatase will transform to rutile. Property of rutile and anatase were shown in table 2.2.

2.4 Applications of Titanium dioxide (TiO_2) for chromium(VI) removal

Parameters influenced the photocatalytic removal of chromium(VI) in the presence of TiO_2 have been studied. For example, Ku and Jung(2001) investigated the reduction of chromium(VI) under various solution pH value, TiO_2 dosages, light intensities, dissolved oxygen levels and other operating condition. The reduction rates of chromium(VI) by photocatalytisis were significantly higher for acidic solutions than alkali solution. Increasing the light intensity would drastically increase the reduction rate of chromium(VI) which, however, was ultimately influenced by the amount of TiO_2 present in solution. The presence of dissolved oxygen had minimum effect on the reduction of chromium(VI) in acidic condition. The presence of ethanol might act as scavenger for holes and promoting the photocatalytic reduction of chromium(VI) by electrons.

Weng et al. (1997) investigated the adsorption of chromium(VI) with TiO_2 as a catalyst. The results showed that the pH of solution was the key factor that effect on adsorption characteristics. The chromium(VI) adsorption was favorable under acidic condition and the adsorbed ability is decreased when increasing pH and surface loading. Besides, decreasing temperature and ionic strength resulted in increasing adsorption capacity.

Schrank et al. (2002) studied the photocatalytic process by illuminate with UV light and used Titanium dioxide as a catalyst for remove chromium(VI) and dye with individual and mixture solution. In the individual solution, the result found that both chromium(VI) and dye were removed in acidic pH. In neutral pH, chromium(VI) can not remove because of chromium(VI) has low efficiency to adsorb on Titanium dioxide. Moreover, in the mixture condition (chromium mixed with dye), chromium have higher removal rate than in the individual solution since dye was oxidized by photo-excited holes which prevented electron-hole recombination and encouraged photoreduction of chromium(VI) on TiO_2. Another that, in the mixture condition dye have higher removal rate than in the individual solution since the result of the prevention of electron-hole recombination by chromium(VI).

Goeringer et al. (2001) found the synergism of photoreduction between two metal ions (copper(II) and chromium (VI)) under UV irradiation of 2 g/L TiO_2. In the absence of 800μM copper(II), chromium(VI) was not completely converted to chromium(III), even after 4 h irradiation. While the presence of 800μM copper(II) resulted in complete chromium(VI) reduction within 20 min. In the same way, the half-life for the photoreduction of 600 μM. Copper(II) decreased from 1 h with no chromium(VI) to 5 min in the presence of 1.6mM chromium(VI).

Watcharenwong (2003) investigated the removal of chromium(VI) from the synthesis wastewater by suspend TiO_2. The parameter emphasis are pH, concentration of chromium(VI) solution, amount of suspended TiO_2 and the effect of another ion which decrease photocatalytic activity. The result showed that, the optimum pH is 3 with 59.4% treatment efficiency. It was found that increasing the concentration of chromium(VI) can decrease k_{obs} value. The reaction rate of this research is pseudo-first-order. Adding of formate ion can increase the efficiency to 82.46%. However, in the other hand, another ions such as chloride, phosphate and sulphate can decrease photocatalytic activity.

2.5 Chitin and chitosan

Chitin is most plentiful natural biopolymer after cellulose and widely distributed throughout nature (Sanford, 1989). The most available sources are the protective shells of crustaceans such as crab and shrimp. In addition, it found in fiberous exoskeleton of insects, in fungal cell walls and other biological materials (Sanford, 1989 and Jeuniaxet et al., 1989).

Chitin is *N*-acetyl-2-aminocellulose or 2-acitamido-2-deoxycellulose and composed of *N*- acetyl-Dglucosamine units link β- D- (1→4) (Whistler, 1993). Chitin existed in three polymorphic forms, that is, α-, β- and γ-chitin (Minke and Blackwell, 1978; Gardner and Blackwell, 1975) with different molecule chains. The crystallographic structure shows the main arrage in an anti-parallel fashion with strong intermolecule hydrogen bonding (Gardner and blackwekk, 1975). Chitin was a highly insoluble material and low chemical reactivity. Its structure is almost the same as that of cellulose. Nevertheless, there is an acetamido group substituting hydroxyl group at C-2 position. Like cellulose, it function naturally as a structural polysaccharide. Chitin is a while, hard, inelastic, nitrogenous polysaccharide and is the major source of surface pollution in coastal areas (Kumar, 2000). It has limited applications because of strong inter- or intra-molecule hydrogen bonding caused by acetamido groups in glucopyranose residues. Nonetheless, solubility, reactivity and process ability of chitin can be improved by chemical modification (Kim et. al., 1994).

Low acetyl forms of chitin composed primarily of glucosamine, 2- amino-3-deoxy-D-glucose, are mainly used (Sanford, 1989; Peniston and Johnson, 1980). Glucosamine and its N-acetylated form are the most abundant amino sugars occurring in polysaccharides, glycoproteins etc (Sanford, 1989). The structures of cellulose, chitin and chitosan were shown in figure 2.6. Chitin and chitosan are of commercial interest due to their high percentage of nitrogen (6.89 %) compared to synthetically substituted cellulose (1.25 %).

Chitosan is a biopolymer produced from N-deacetylation of chitin, a major component of crustacean shells, and is readily available from seafood-processing wastes. Chitosan has widely been used in the preparation of various biomedical products. Chitosan could be defined as sufficiently deacetylated chitin to form soluble amine salts. To obtain a soluble product, the degree of deacetylation must be 80 to 85 % or higher. The content of acetyl groups in chitosan products must be less than 4-4.5 %. Chitosan products were highly viscous (Penision and Johnson, 1980).

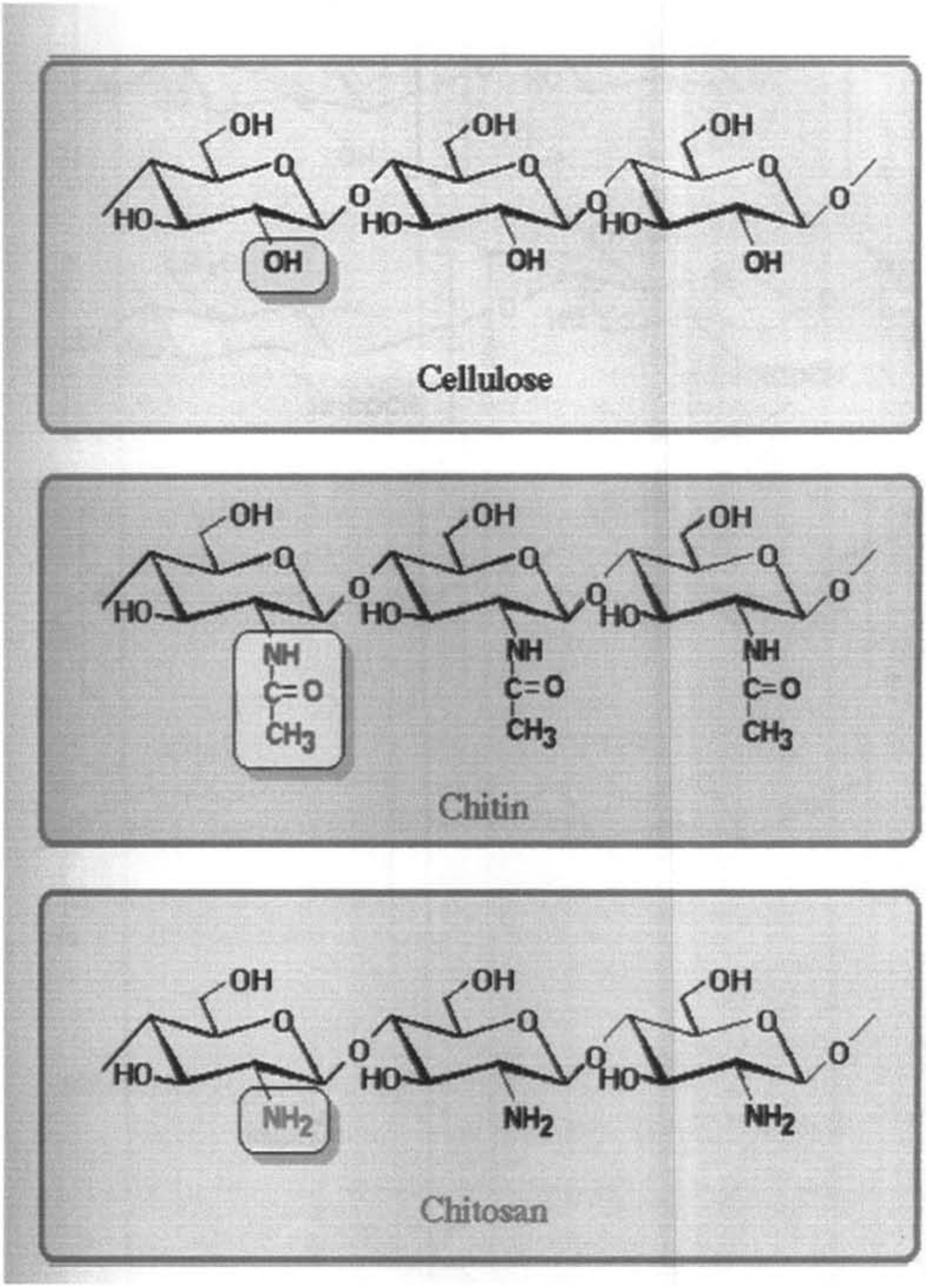


Figure 2.6 Chemical structure of cellulose, chitin and chitosan (Sappawinyoo, 2002)

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The possibility of using chitosan as a material to remove organic pollutants from water. However, It is not commonly explored. Since the deacetylated amino groups in chitosan can be protonated, the polycationic properties of the polymer can be expected to contribute to the charged interactions with anionic substances. Chitosan has been reported to have high potential for adsorption of metal ions, dyes and proteins (Zeng, 1998). Chitosan is a powerful chelating agent, which is easy to form complexes with transition metals and heavy metals. Recent years, most researches of chitosan derivatives-metal complexes focused on their applications in the sequestration or removal of metal ions, dyeing, catalysis, water treatment, and many other industrial processes(Ding et al., 2006).

2.5.1 Chemical and physical properties of chitosan

Although the molecule structures of chitin and chitosan are rather similar, their chemical reaction and physical properties are different. Both compounds possess reactive hydroxyl and primary amine groups but chitosan is less crystalline than chitin (Winterowd and Sandford, 1997).

2.5.1.1 Common Organic Reaction

Chitin and chitosan are considered as weak bases and undergo the typical neutralization reactions of alkaline compounds. Chitosan is insoluble in alkaline aqueous solution. Presumably, the multitude of cationic site along the chain allows for the water solubility by increasing both the polarity of the compound and degree of polymer-to-polymer electrostatic repulsion. Evidently, chitin possesses an insufficient percentage of glucosamine units to permit water solubility, even under acidic conditions (Winterowd and Sanford, 1997).

Chitin and chitosan were suspectible to acid- or base-catalyzed hydrolysis. Under acidic or alkaline conditions, acetic acid could be liberated as the N-acetyk groups at C2 are converted to primary amine (Muzzarelli, 1997). Acidic conditions also result in some degree of depolymerization as hydrolysis of the β-glycosidic linkages takes place (Madhaven and Ramachandran, 1974). Depolymerization occurs in the low alkaline environments. Normally, chitosan could be degraded by treatment with nitrous acid (Allan and Peyron,1989).

2.5.1.2 Heavy Metal Complexes

The free doubles of nitrogen atoms and possibly those of oxygen atom beard by the two kind of monomers can be use to elaborate interactions of chelate type with numerous metals. Uptake of metals such as Hg, Cd, Pb, Zn, Ni, Cr, Cu, Fe, Mn, Ag, and Pt in chitosan has been reported in the range between 0.5-5.0 meq/l chitosan (Ratananonchai, 1998). There have been several reports on the interactions of chitin and chitosan with metals (Yaku, 1978; Skaugrund 1989 and Chui et. al., 1996). Complexes do not form between these polymers and metals in groups 1 or 2 (Winterowd and Sanford, 1997). The tenancy of chitin and chitosan to form complexes with heavy metals has significant impact on their toxicity. Severe toxicity could occur if chitosan contaminated with or lead was consumed and the heavy metal release into the intestinal tract (Winterrowd and Sandford, 1997).

2.5.1.3 Enzymatic Reactions

Chitin and chitosan are degraded by lysozyme under the proper conditions of temperature, ionic strength and pH (Sashiwa et al., 1989 and Kumar, 2002). Hydrolysis by chitinase, chitosanase, lysozyme and other enzymes could also occur (Winterowd and Sanford, 1997).

To taken orally, chitin and chitosan are considered to be essentially nondigestible by human because there is no bacterial in gut flora of human that possesses chitinases or chitosanases, whereas animals, such as fish, hens and rabbits are capable to digest chitin or chitosan (Hirano et.al., 1990 and Winterowd and Sanford 1997,). Low concentration of lysozyme is found in the saliva and the stomach fluids of human (Hirano et al., 1990). The enzyme, nevertheless, degrades a small extent of chitin or chitosan. Hydrolytic degradation could also occur in the stomach at pH between 1 and 2 (Winterword and Sandford, 1997).

2.5.1.4 Solubility

The solubility of chitosan in water depends on the balance between the electrostatic repulsion occurring at protonated amine functions and the hydrogen bounding due to the free amino groups. The upper limit of pH for solubility depends on the value of pK_a (Domard and Rinaudo, 1989). In the free amine form, chitosan is not soluble in water at neutral condition but in acidic condition amino groups in chitosan are protonated to form cationic amine groups and become soluble (Sanford, 1989). The solubility is observed when pH is lower than 6 or 5.5 (Domard and Rinaudo, 1989). Chitosan is insoluble in sulfuric acid and phosphoric acid while other mineral acids such as hydrochloric, nitric, and perchloric acid dissolve chitosan. Solubility of chitosan is, however, enhanced in organic acids such as acetic, lactic, propionic, formic and citric acid (Muzzareli, 1977). Commonly, acetic acid is used as a reference for solubility of chitosan (Domard, 1996; Sitthai, 1994 and Park et.al., 2002).

2.5.1.5 Viscosity

Just as with other food matrices, viscosity is an important factor conventional determination of molecular weight of chitosan and in determining its commercial application incomplex biological environments such as in the food system (Muzzareli, 1977). Higher molecule weight chitosans often render highly viscous solutions, which may not be desirable for industrial handling. Some factors during processing such as the degree of deacetylation, molecule weight, concentration of solution, ionic strength, pH, and temperature affect the production of chitosanand its properties (Moorjani et al., 1978). For instance, chitosan viscosity decreases with an increased time of demineralization (Moorjani et al., 1978). Viscosity of chitosan in acetic acid tends to increase with decreasing pH but decrease with decreasing pH in HCl, giving rise to the definition of "Intrinsic Viscosity" of chitosan which is a function of the degree of the degree of ionization as well as ion strength (Muzzarelli, 1977).

2.6 Equilibrium adsorption isotherms

2.6.1 Langmuir adsorption isotherm

It is the most commonly used adsorption model described by the following this equation:

$$C_e/(x/m) = 1/(Q_o b) + C_e/Q_o \qquad \text{(Eq. 2.1)}$$

Where C_e is the equilibrium concentration of solution, mg/L, x/m is the amount of solute adsorbed at equilibrium per unit mass of adsorbent, mg/g, Q_o is the maximum adsorption at monolayer coverage, mg/g and b is the Langmuir constant related to the affinity of binding sites, L/mg and is a measure of the energy of adsorption.

In a two-component system consisting of sorbent and solution, a plot of the solute concentration in the solid phase x/m as function of the solute concentration in the solution C_e at equilibrium gives an adsorption isotherm. In a solid liquid system, the adsorption results in the removal of solute from the solution onto solid surface until the remaining solute in the solution is in dynamic equilibrium with solute on the solid surface. At equilibrium there is a finite distribution of the solute between the liquid and solid phases, which can be described by many isotherms and adsorption models can be used to fit the observed experimental data and determine the model parameters.

2.6.2 Freundlich adsorption isotherm

Freundlich isotherm assumes that the uptakes of metal ions occur on a heterogeneous surface by multiplayer adsorption and that the amount of solute adsorbed increases infinitely with increase in the concentration. The Freundlich isotherm is described by the following this equation

$$Log(x/m) = (1/n)\log C_e + \log k_f \qquad \text{(Eq. 2.2)}$$

Where C_e is the equilibrium concentration of solution, mg/L, x/m is the amount of solute adsorbed at equilibrium per unit mass of adsorbent, mg/g and n and k_f are Freundlich constant which are the measure of adsorption intensity and adsorption capacity, respectively.

2.7 Applications of chitosan for chromium(VI) removal

Ramnani et al. (2005) studied the adsorption of chromium(VI) onto crosslinked chitosan synthesized. The adsorption behavior of crosslinked chitosan (CRC) and its hydrolysis product (CRCH) has been compared with native chitosan. The result shown that maximum adsorption of chromium(VI) on crosslinked chitosan occurs at pH 3. The results obtained from equilibrium adsorption studies are fitted in various adsorption models such as Langmuir, Freundlich and the model parameters have been evaluated. The performance of crosslinked chitosan (CRC and CRCH) under flow conditions have also been studied and the results indicates that radiation crosslinked chitosan can be effectively used for treating wastewater containing chromium(VI).

Sankararamakrishnan et al. (2005) modified chitosan as highly efficient adsorbent for the recovery of toxic chromium(VI) was studied. After cross linking with glutaraldehyde, xanthate group was grafted onto the back bone of chitosan. The sorption was found to be both pH and concentration dependent, with pH 3 being the optimum value. Both chemically modified beads (CMCB) and flakes (CMCF) followed a pseudo-second-order kinetics with a rate constant of 2.037 and 4.639 g.min/mg, respectively. The equilibrium data followed the Langmuir isotherm model with maximum capacities of 625 mg/g and 256.4 mg/g and for CMCF and CMCB respectively.

Rojas et al. (2005) investigated adsorption of chromium onto cross-linked chitosan that was realized by means of analysis of pH influence, particle size, adsorbent weight. As concentrations of chromium in solution in this paper are determined by colorimetric method with diphenylcarbazide. Optimum pH of chromium(VI) adsorption is 4.0 while chromium(VI) is partially reduced in the range pH≤3.0. The high capacity developed with chromium(VI) is 215 mg/g due to highly protonated active sites in the acidic range of pH. Equilibrium data fit to both Langmuir and Freundlich isotherms.