THE REMOVAL OF ZINC AND PLUMBUM (LEAD) BY USING HYDROGEN PEROXIDE

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A thesis submitted in fulfillment of the requirements for the award of the degree of Bachelor of Chemical Engineering

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I declare that this thesis entitled “*The removal of zinc and plumbum (lead) by using hydrogen peroxide*” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and not concurrently submitted in candidature of any other degree.

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ABSTRACT

Protection of ground-water and marine waters is a complex issue and a vital public concern. Once contaminated, it can be technically difficult and enormously expensive to clean up. One way to protect these waters from contamination is through the control of industrial discharges. Often though, control processes are not practical in treating high flow rates or those with relatively low contaminant concentrations. This proposal involves a process for removing heavy metals from wastewater streams using hydrogen peroxide. The specific contaminant addressed in this research are zinc and lead removal, which has become a serious concern because of its toxicity to human, animal and aquatic life. The main objective of this research is to study the effectiveness of hydrogen peroxide in the removal of heavy metal ions from wastewater. The scopes of this experiment are to determine the effect of hydrogen peroxide concentration and the effect of pH in order to get maximum removal heavy metal ions in wastewater. This experiment started by determining the concentration of hydrogen peroxide that has the maximum removal. Then the concentration of hydrogen peroxide is used to add to each five wastewater sample. Next, all samples were set to different pH which are 4, 6, 8, 10 and 12. At the end of this research, it was observed that the maximum removal of heavy metal was found to be at 30% v/v of hydrogen peroxide and at pH 8. The amount of lead and zinc reduced are 95.28% and 80.4%, respectively.

ABSTRAK

Pemeliharaan air bawah tanah dan air marin adalah suatu isu yang rumit dan merupakan perkara yang sering mendapat perhatian masyarakat. Sekali ia dicemari, ia akan menjadi masalah teknikal dan terlalu mahal untuk dibersihkan. Salah satu cara untuk memelihara air daripada pencemaran adalah menerusi kawalan ke atas pembuangan sisa daripada industri. Meskipun kerap, proses kawalan adalah tidak praktikal dalam rawatan pada kadar pengaliran yang tinggi atau pada air yang kandungan bahan cemarnya adalah rendah. Cadangan ini melibatkan proses penyingkiran logam berat daripada air sisa mengunakan hidrogen peroksida. Bahan cemar yang khusus digunakan dalam kerja ini adalah penyingkiran zink dan plumbum, di mana ianya telah menjadi tumpuan yang serius kerana kandungan toksiknya yang berbahaya ke atas manusia, haiwan dan hidupan laut. Tujuan utama penyelidikan ini adalah untuk mempelajari keberkesanan hidrogen peroksida dalam penyingkiran ion logam berat daripada air sisa. Skop kajian ini ialah untuk menentukan kesan kepekatan hidrogen peroksida dan kesan pH bagi penyingkiran ion logam berat yang maksimum daripada air sisa. Ujikaji dimulakan dengan menentukan kepekatan hidrogen peroksida yang mempunyai penyingkiran yang terbanyak. Seterusnya kepekatan hidrogen peroksida yang telah diperolehi akan digunakan ke atas setiap lima sampel sebelum ditetapkan dengan pH yang berbeza iaitu 4, 6, 8, 10, dan 12. Di akhir kajian ini, keputusan yang diperoleh di mana penyingkiran ion logam yang maksimum adalah pada 30% v/v hidrogen peroksida dan pada pH 8. Jumlah plumbum dan zink yang disingkirkan adalah 95.28% dan 80.4%.

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mL - Milliliter

ppm - Part per million (mg/L)

L - Liter

mg - Milligram

ABS - Absorbance

Rpm - Rotation per minute

^{o}C - degree Celsius

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CHAPTER 1

INTRODUCTION

1.1 Background of study

One of the main causes of industrial pollution is the discharge of effluents containing heavy metals. Heavy metals can have serious effects not only on human and animal health but also on aquatic life. Beside the health effects, heavy metals are nonrenewable resources. Therefore, effective recovery of heavy metals is as important as their removal from waste streams. Disposal of industrial wastewater has always been a major environmental issue. Pollutants in industrial wastewater are almost invariably so toxic that wastewater has to be treated before its reuse or disposal in water bodies. Industrial processes generate wastewater containing heavy metal contaminants. Since most of heavy metals are non-degradable into non-toxic end products, their concentrations must be reduced to acceptable levels before discharging them into environment. Otherwise these could pose threats to public health and/or affect the aesthetic quality of potable water. According to World Health Organization (WHO) the metals of most immediate concern are chromium, zinc, iron, mercury and lead (WHO, 1984). Maximum allowed limits for contaminants in “treated” wastewater are enforced in developed and many developing countries. The treatment of contaminated waters is as diverse and complicated as the operation from which it comes. A number of conventional treatment technologies have been considered for treatment of wastewater contaminated with heavy metals.

Previous investigations on the removal of heavy metals from wastewater (Howari and Garmoon, 2003; Shwarts and Ploethner, 1999; El-Awady and Sami, 1997) suggest that systems containing calcium in the form CaO or $CaCO_3$ and carbonates in general, are particularly effective in the removal of heavy metals from wastewater. Some of the conventional techniques for removal of metals from industrial wastewater include chemical precipitation, adsorption, solvent extraction, membrane separation, ion exchange, electrolytic techniques, coagulation/flotation, sedimentation, filtration, membrane process, biological process and chemical reaction (Blanco *et al*., 1999; Blanchard *et al*., 1984; Gloaguen and Morvan, 1997; Jeon *et al*., 2001; Kim *et al*., 1998; Lee *et al*., 1998; Mofa, 1995; Lujan *et al*., 1994; Gardea-Torresdey *et al*., 1996). Each method has its merits and limitations in application. Similarly, hydrogen peroxide (H_2O_2) has been used in different experiments to improve supply and oxidation rate of suspended and dissolved particles that cause pollution in such water effluent (Bami, 1989; Muganlinskii and Adeyinka, 1987; Adeyinka, 1996; Adeyinka and Rim-Rukeh, 1999; Chen 1996).

1.2 Problem statement

Great importance has been attached to the treatment of industrial wastewater effluent since local and international authorities require that wastewaters from industries be treated and made to meet a set standard before it is discharged into the water bodies. Chemical treatment of industrial wastewater is preferable since industrial wastewaters are frequently complex, high in pollutant load and often containing materials toxic or resistant to the organisms on which biological processes depend. Also, chemical treatment systems are more predictable and inherently more subject to control by simple technique and chemicals are usually relatively tolerant to temperature changes. In the chemical treatment of wastewater, the use of hydrogen peroxide has gained much popularity. Hydrogen peroxide (H_2O_2) is a powerful oxidizer that looks like water in its appearance, chemical formula and reaction products. In addition, it is stronger oxidizer compared chlorine, chlorine dioxide, and potassium permanganate. Besides that, through catalysis, H_2O_2 can be converted into hydroxyl radical (OH^-) with reactivity second only to fluorine (Badmus, 2007). Despite its power, it is a versatile oxidant which is both safe and effective.

1.3 Objective of the Study

The main objective of this study is to identify the effectiveness of hydrogen peroxide in the removal of heavy metal ions in wastewater.

1.4 Scopes of experiment

The scopes of this experiment are:

(a) Determine the effect of hydrogen peroxide concentration in the removal of heavy metal ions which are, ion zinc (Zn^{2+}) and ion lead (Pb^{2+})

(b) Determine the optimum removal of ion zinc (Zn^{2+}) and ion lead (Pb^{2+}) at various pH.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy metals pollution in water

Heavy metal pollution is a quickly growing problem in oceans, lakes, and rivers (aquatic). But only a relatively small number of heavy metals such as cadmium, lead, zinc, copper, iron, cobalt, mercury, vanadium, nickel, chromium, manganese, molybdenum, silver, and tin as well as the metalloids arsenic and selenium are associated with environmental, plant, animal, or human health problems.

Even though the chemical forms of heavy metals can be changed, they are not subject to chemical or biological destruction. Therefore, after release into the environment they are persistent contaminants. Natural processes such as bedrock and soil weathering, wind and water erosion, volcanic activity, sea salt spray, and forest fires release heavy metals into the environment. While the origins of anthropogenic releases of heavy metals are lost in antiquity, they probably began as our prehistoric ancestors learned to recover metals such as gold, silver, copper, and tin from their ores and to produce bronze. The modern age of heavy metal pollution has its beginning with the Industrial Revolution. The rapid development of industry, intensive agriculture, transportation, and urbanization over the past 150 years, however, has been the precursor of today's environmental contamination problems (El-Awady MH, Sami TM,1997).

Anthropogenic utilization has also increased heavy metal distribution by removing the substances from localized ore deposits and transporting them to other parts of the environment. Heavy metal by-products result from many activities including: ore extraction and smelting, fossil fuel combustion, dumping and landfilling of industrial wastes, exhausts from leaded gasolines, steel, iron, cement and fertilizer production, refuse and wood combustion (E. Oliveros, O. Legrini, M. Hohl, T. Muller, A.M. Braun, 1997).

Water sources that are near factories and manufacturing plants may be contaminated with heavy metals like mercury, zinc, lead, cadmium, iron, magnesium and aluminum. If the metals attach to the sediment, they may find their way into the food chain via plants and aquatic animals. The end result is heavy metal poisoning if the concentration in the water is high enough. Making polluted water fit for consumption and use again is not an easy process. No one purification or filtration method works for all types of water pollution. In order to make water usable again after water pollution, it must be treated with a variety of filtration and purification methods.

2.2 The heavy metals poisoning

Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources.

Heavy metals are dangerous because they tend to bio-accumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater. Now we are going to describe the kinds of heavy metals, their dangerous levels and the effects of these heavy metals to human health and environment. The most pollutants heavy metals are lead, zinc, cadmium, copper, chromium, selenium and mercury. Human exposure to lead, especially at a young age, impairs a range of neurological functions. The symptoms of lead poisoning vary with dose, and include cognitive decline, hyperactivity, and anemia. Besides that, long term exposure can occur, acute or chronic damage to the nervous system on humans. The free zinc ion in solution is highly toxic to plants, invertebrates, and even vertebrate fish. Copper is an essential substance to human life, but in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation. Cadmium In humans, long-term exposure is associated with renal disfunction. High exposure can lead to obstructive lung disease and has been linked to lung cancer, and damage to human’s respiratory systems. Effect of the mercury is to cause damage to the brain and the central nervous system. Chromium is used in metal alloys and pigments for paints, cement, paper, rubber, and other materials. Low-level exposure can irritate the skin and cause ulceration. Long-term exposure can cause kidney and liver damage, and damage too circulatory and nerve tissue. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium. Selenium causes to damage to circulatory tissue, and more severe damage to the nervous system. Mercury causes damages to the brain and the central nervous system, causes psychological changes and makes development changes in young children. Normally mercury is a toxic substance which has no known function in human biochemistry (Gloaguen V, Morvan H, 1997).

2.3 Metal treatment by hydroxide precipitation in industry

As metals enter the treatment process, they are in a stable, dissolved aqueous form and are unable to form solids. The goal of metals treatment by hydroxide precipitation is then to adjust the pH (hydroxide ion concentration) of the water so that the metals will form insoluble precipitates. Once the metals precipitate and form solids, they can then easily be removed, and the water, now with low metal concentrations, can be discharged.

Metal precipitation is primarily dependent upon two factors: the concentration of the metal, and the pH of the water. Heavy metals are usually present in wastewaters in dilute quantities (1 - 100 mg/L) and at neutral or acidic pH values (< 7.0). Both of these factors are disadvantageous with regard to metals removal. However, when one adds caustic to water which contains dissolved metals, the metals react with hydroxide ions to form metal hydroxide solids:

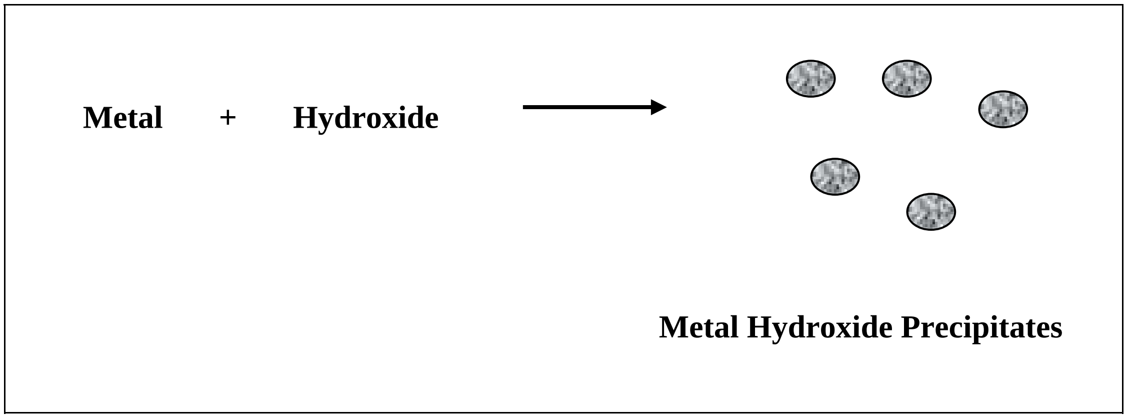

Figure 2.1: The reaction of metal with hydroxide

2.3.1 Unit Operations of Wastewater Treatment in Industry

Metal removal occurs through the use of several unit operations, as displayed in figure 2.2 below. This figure also shows the points in the treatment process where the pH must be adjusted to insure adequate metals and metals solids removal.

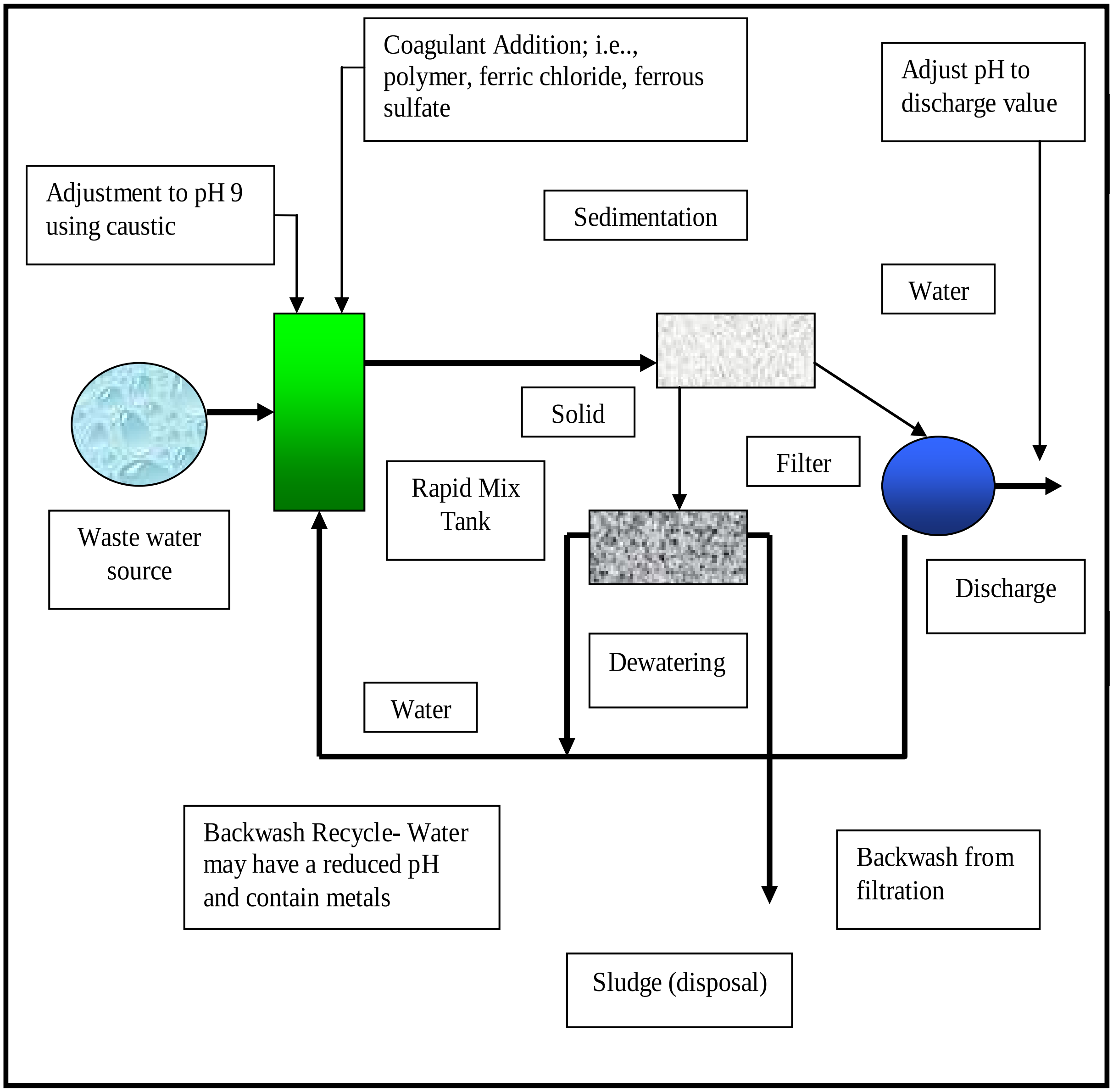

Figure 2.2: The Processes of a Conventional Metals Precipitation Treatment Plant

2.4 Chemical processes of heavy metal removal

Various techniques have been developed to remove the heavy metals from wastewater. Conventional techniques used for example solvent extraction, electrolysis, evaporations, cementation, flotation and stripping are limited to process small volumes of water at high concentrations of metal ions. Many technologies are used today to treat large volumes of diluted metal ion-containing solution i.e. reverse osmosis, membrane filtration, ion exchange and adsorption. However, these processes are very expensive and require high level of expertise to operate and maintain the process.

2.4.1 Adsorption

These are the most widely used techniques in wastewater treatment process. Activated carbon, silica sand, coal and alumina are usually used as an adsorbent. The effectiveness of an adsorbent depends on the adsorptive properties of their surface. Adsorption takes place when a solid surface is contacted with a solution and tends to accumulate a surface layer of solute molecules created by the unbalance surface forces. Activated carbon have been reported to remove heavy metals such as Pb^{2+}, Zn^{2+}, Hg^{+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, $Cr^{3+}$and Mn^{2+} (de Oliveira, E. and Yabe, 2001). However, from the different types of activated carbon found commercially, very few are selective for heavy metals and are also very costly.

Adsorption is a process in which matter is extracted from one phase and concentrated at the surface of a second (a surface phenomenon). Surface reactions of this type must occur at least partly as a result of the forces within the phase boundaries or surface boundaries. Surface tensions are the development of a tension at the surface which tends to keep a water drop from spreading a thin flat layer, resulting from attractive forces between molecules of water within the drop. Molecules of water are attracted to one another by cohesion forces more strongly than they are by adhesion forces to molecules of the solid plate or molecules of air at the gas-liquid, or liquid-solid interfaces. Enlarging a surface requires the breaking of bonds between molecules making up the liquid phase, and the forming of bonds between molecules of different phases. Hence, to increase the surface of a liquid requires an input of work in excess of that necessary to merely compensate the tension at the surface (Kim SJ, Jeung SY and Moon H,1998).

2.4.2 Ion exchange

Ion exchange is a reversible chemical reaction wherein an ion (an atom or molecule that has lost or gained an electron and thus acquired an electrical charge) from solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. An organic ion exchange resin is composed of high-molecular-weight polyelectrolytes that can exchange their mobile ions for ions of similar charge from the surrounding medium. Each resin has a distinct number of mobile ion sites that set the maximum quantity of exchanges per unit of resin. Most of the resins used are synthetic because their characteristics can be tailored to specific applications. Synthetic resin made by polymerization of organic compounds in a porous three-dimensional structure. Ion exchange resins are classified as cation exchangers, which it have positively charged mobile ions available for exchange, and anion exchangers, whose exchangeable ions are negatively charged. Both anion and cation resins are produced from the same basic organic polymers. They differ in the ionizable group attached to the hydrocarbon network. It is this functional group that determines the chemical behavior of the resin. Resins can be broadly classified as strong or weak acid cation exchangers or strong or weak base anion exchangers (Patterson and J.W.,2005). For the purpose of heavy metal removal, a polystyrene matrix type resin with a chelating functional group is widely used. The disadvantage of using the heavy-metal-selective chelating resins is their high cost. Ion exchange is not practical to handle multiple waste streams due to the high selectivity of resin.

2.4.3 Reverse Osmosis (RO)

The reverse osmosis process depends upon a semi-permeable membrane through which pressurized water is forced. Reverse osmosis, simply stated, is the opposite of the natural osmosis process of water. Osmosis is the name for the tendency of water to migrate from a weaker saline solution to a stronger saline solution, gradually equalizing the saline composition of each solution when a semi-permeable membrane separates the two solutions. In reverse osmosis, water is forced to move from a stronger saline solution to a weaker solution, again through a semi-permeable membrane. Because molecules of salt are physically larger than water molecules, the membrane blocks the passage of salt particles. The end result is desalinated water on one side of the membrane and a highly concentrated, saline solution of water on the other side (Mcvaugh, J. and Wall, W.T.,1996). In addition to salt particles, this process will remove a select number of drinking water contaminants, depending upon the physical size of the contaminants. For this reason, reverse osmosis has been touted as an effective drinking water purification method.

2.4.4 Membrane Filtration

Membrane filtration is the process of separating mixtures of materials depending on the particle size. When used for wastewater treatment, membrane filtration processes offer a high level of purification allowing the wastewater to be recovered and re-used. Moreover, the technology offers a low footprint and has relatively low energy consumption. The quantity of water reused and/or recycled, at a particular site, is dependent on the level of treatment, which is directly related to the characteristics of the site effluent and the application required for the treated water. Typical reuse and recycle efficiencies obtained by membrane filtration processes range up to 90% depending on application. Typically, a complete ‘system’ for wastewater treatment, recovery and re-use using membrane technology consists of a feed tank, permeate and reject handling facilities, monitoring and control units and a cleaning in place system. Pre- and post-treatment may also be incorporated into the process depending on the level of quality required for re-use (Mcvaugh, J. and Wall, W.T.,1996).

2.5 Chemical Treatment by using Hydrogen Peroxide

One of the conventional technologies of wastewater treatment is by using hydrogen peroxide. It has been widely used all over around the world. The production of hydrogen peroxide has been grown up over billion pounds per year.

2.5.1 Chemical precipitation reaction

Chemical precipitation is the most common technology used to remove dissolved (ionic) metals from solutions, such as process wastewaters containing toxic metals. The ionic metals are converted to an insoluble form (particle) by the chemical reaction between the soluble metal compounds and the precipitating reagent. The particles formed by this reaction are removed from solution by settling and or by filtration. The unit operations typically required in this technology includes neutralization, precipitation, coagulation or flocculation, solids or liquid separation and dewatering. The effectiveness of a chemical precipitation process is dependent on several factors, including the type and concentration of ionic metals present in solution, the precipitant used, the reaction conditions (especially the pH of the solution and temperature), and the presence of other constituents that may inhibit the precipitation reaction (presence of catalyst). Metal hydroxides are amphoteric (such as $Zn(OH)_2$, $Pb(OH)_2$, $Cd(OH)_2$, $Al(OH)_3$) which means they are increasingly soluble at both low and high pH values (Capaccio, R. S., 1996). Therefore, the optimum pH for precipitation of one metal may cause another metal to solubilize, or start to go back into solution.

2.5.2 Precipitation by pH

To convert dissolved (ionic) metals into insoluble particles, the traditional method is to adjust the pH of the solution using caustic, such as sodium hydroxide. The precipitating reaction forms metal hydroxides. The results obtained are affected by several conditions, one of which is the pH of the solution. Every dissolved metal has a distinct pH at which the optimum hydroxide precipitation will occur, for example, zinc at pH 8.1, lead at pH 8.0-8.5, copper at pH 7.8, chromium at pH 7.5, nickel at pH 10.8, cadmium at pH 11.0 (WST, 2003). Since metal hydroxides are quite soluble, many such hydroxides will start to go back into solution if the pH changes even slightly. For example, lead can generally be precipitated as a lead hydroxide at a pH of 8.0-8.5. When the pH rise to above 8.5, lead hydroxides become soluble. Same thing goes for other types of heavy metal. Thus, it is important to identify the pH for each heavy metal where the optimum hydroxide precipitate will occur.

2.6 Zinc

The two most common forms of zinc are the amorphous form and the $Zn(OH)_2$ form. The reported water solubility of zinc hydroxide ranges from 2.92 mg/L (18 ^{o}C) to 15.5 mg/L (29 ^{o}C) (Pourbaix, 2004). These variations in solubility data are most likely due to variations in the solubility tests with respect to the form of zinc used, oxide or hydroxide (the amorphous form of zinc hydroxide is more soluble), pH, temperature, and experimental variability. Zinc hydroxide is insoluble in organic solvents, including alcohols and acetone. Zinc hydroxide is amphoteric; they dissolve in acids to form salts and in alkalis to form zincates (above pH 7).

In water, zinc ion may associate or react with neutral or ionic compounds to form inorganic salts, stable organic complexes, or inorganic or organic colloids. The quantity of zinc ion available in water from each of these forms is dependent upon the solubility of these forms, pH, temperature, the total amount of the zinc form present in water, and the presence of other metal ions, organic compounds, and inorganic compounds. Zinc ion exhibits high toxicity to aquatic organisms. Numerous studies indicate that zinc ion also has a high chronic toxicity. For example, the aquatic toxicity is the availability evidence indicates that zinc ion is highly toxic to aquatic organisms and has a high potential to bioaccumulate.

In natural waters, zinc ion occurs in both suspended and dissolved forms. It can exist as a simple hydrated ion; as various inorganic salts; in stable organic complexes; or adsorbed into or occluded in, inorganic or organic colloids. The quantity of zinc ion available from each of these forms is dependent upon pH, temperature, and the total amount of the zinc form present in water, and the presence of other metal ions or organic and inorganic compounds. Zinc is eventually partitioned into sediments. Zinc ion bioavailability from sediments is enhanced under conditions of high dissolved oxygen, low salinity, low pH, and high levels of humic substances. Zinc ion remaining in sediments may be toxic to or bioaccumulate in sediment organisms. The levels of acute toxicity for zinc ion to various fish and invertebrates range from 40 ppb to 58,100 ppb (Patterson, 2005). This wide range is partially due to the hardness of the water used in the studies; generally as water hardness increases the acute toxicity of zinc ion decreases.

2.7 Plumbum (Lead)

Lead compounds are generally soluble in soft, slightly acidic water. Lead waterworks were often applied in former days, and these may still be present in old buildings. Lead from pipes may partially dissolve in the water flowing through. Lead may bind to carbonate, therefore lower amounts of lead dissolve in hard water. Inside the pipes, a layer of hardly soluble alkalic lead carbonate is formed. This layer functions as a protective coating for the underlying lead of the pipes. The Romans often filled the pipes with wine on holidays, causing the layer to dissolve and form lead sugar. Despite its toxicity, the above-mentioned lead (II) acetate was applied far into the 19th century, to sweeten wine and other beverages and food stuffs. Lead white, an alkalic lead carbonate ($2PbCO_3 \cdot Pb(OH)_2$), is a white pigment (Shwarts MD and Ploethner D 1999). It is no longer applied because of its extreme toxicity. Organic lead is applied in petroleum production, and inorganic lead compounds are applied for battery and paint production. Most industrially processed lead is applied for fabricating computer and TV screens. The lead compound tetra-ethyl lead is applied as an additive in fuels. This organic lead compounds is quickly converted to inorganic lead, and ends up in water, sometimes even in drinking water. Fortunately, this form of release of lead is less and less abundant. In architecture lead is applied in roofs and in stained glass windows. Generally, lead dissolved or suspended in wastewater mostly stems from streets, pipes and soils.

2.7.1 Health effect of lead in water

The human body contains approximately 120 mg of lead. About 10-20% of lead is absorbed by the intestines (R.E. Clement, G.A. Eiceman and C.J. Koester, 1995). Symptoms over overexposure to lead include colics, skin pigmentation and paralysis. Generally, effects of lead poisoning are neurological or teratogenic. Organic lead causes necrosis of neurons. Inorganic lead causes axonal degeneration and demyelination. Both species of lead may cause cerebral oedema and congestion. Organic lead compounds are absorbed quicker, and therefore pose a greater risk. Organic lead derivates may be carcinogenic. Women are generally more susceptible to lead poisoning than men. Lead causes menstrual disorder, infertility and spontaneous abortion, and it increases the risk of stillbirth. Foetuses are more susceptible to lead poisoning than mothers, and generally foetuses even protect mothers from lead poisoning. A long time ago lead was applied as a measure of birth control, for example as a spermicidal, and to induce abortion. Children may absorb a larger amount of lead per unit body weight than adults (up to 40%). Consequently, children are generally more susceptible for lead poisoning than adults. Symptoms include lower IQs, behavioural changes and concentration disorder. Lead accumulates in leg tissue. The most severe type of lead poisoning causes encephalopathy. Lead toxicity is induced by lead ions reacting with free sulfydryl groups of proteins, such as enzymes. These are deactivated. Furthermore, lead may interact with other metal ions (World Health Organization, 1984).

2.8 Hydrogen peroxide

As simple as it may seem, the treatment of contaminated waters is as diverse and complicated as the operations from which it comes. In today's environment, where merely transferring contaminants from one medium to another is no longer acceptable, it is no surprise that a powerful oxidizer that looks like water in its appearance, chemical formula and reaction products should be so widely used.

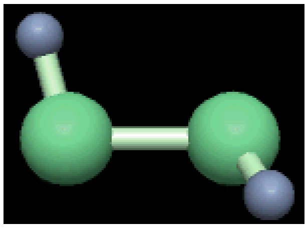

Figure 2.3: Hydrogen peroxide molecule

This is hydrogen peroxide (H_2O_2) a powerful yet versatile oxidant that is both safe and effective. H_2O_2 is one of the most powerful oxidizers known. It is stronger than chlorine, chlorine dioxide, and potassium permanganate. And through catalysis, H_2O_2 can be converted into hydroxyl radicals ($^{\cdot}OH$) with reactivity second only to fluorine. It reacts selectively with contaminants, and by adjusting reaction parameters (e.g., pH, temperature, concentration, reaction time, and/or catalyst addition), H_2O_2 can often be made to oxidize one pollutant over another, or even to favor different oxidation products from the same pollutant. Besides that, by adding a catalyst, the selectivity can be more easily controlled. Also, because partial oxidation can sometimes reduce toxicity to acceptable levels, less than stoichiometric amounts of hydrogen peroxide can often do the job. In commercial storage, hydrogen peroxide is quite stable, with a natural decomposition rate of less than 1 % per year (Muganlinskii and Adeyinka, 1997).

2.8.1 H_2O_2 Processes

2.8.1.1 Simple H_2O_2

Most H_2O_2 applications involve its simple injection into the water stream with no requirement for additional chemicals or equipment. These include the control of biogrowth (slime), the supply of supplemental oxygen, the removal of FOG (fats, oils and grease) and chlorine residuals, and the oxidation of sulfides/sulfites, metals, and other easy-to-oxidize components of BOD/COD (Biochemical/Chemical Oxygen Demand). Activation of H_2O_2 in these applications may be affected by the adjustment/control of pH, temperature, and/or reaction time.

2.8.1.2 Catalytic H_2O_2

The more difficult-to-oxidize pollutants may require the H_2O_2 to be activated with catalysts such as iron, copper, manganese, or other transition metal compounds. These catalysts may also be used to speed up H_2O_2 reactions that may otherwise take hours or days to complete. H_2O_2 catalysis may occur either in solution (using soluble catalysts) or in packed columns (using solid catalysts). If H_2O_2 works as solution catalyst, the most commonly used solution catalyst is iron, which when used with H_2O_2 is referred to as Fenton's Reagent. The reaction requires a slightly acidic pH and results in the formation of highly reactive hydroxyl radicals ($^{\cdot}OH$) which are capable of degrading most organic pollutants. Another solution catalyst is copper, which is often used to destroy cyanides. Other metals also show catalytic activity with H_2O_2 and may be used to selectively destroy specific pollutants. When it works as solid catalyst, it will eliminate the need to add soluble metals to the waste stream, and may offer greater flexibility in terms of reaction rates, selectivity, and the need for pH adjustment. This is an active area of research and many new developments are underway for a variety of applications.

2.8.1.3 Advanced Oxidation Processes (AOP's)

AOP's represent the newest development in H_2O_2 technology, and are loosely defined as processes that generate highly reactive oxygen radicals without the addition of metal catalysts. Typically, this means combining H_2O_2 with ozone or ultraviolet light. The result is the on-site total destruction of even refractory organics without the generation of sludges or residues. This technology is being widely applied to treat contaminated groundwater, to purify and disinfect drinking waters and process waters, and to destroy trace organics in industrial effluents.

2.8.2 H_2O_2 Advantages

H_2O_2 is one of the most powerful oxidizers known; it is stronger than chlorine, chlorine dioxide, and potassium permanganate. And through catalysis, H_2O_2 can be converted into hydroxyl radicals ($^{\cdot}OH$) with reactivity second only to fluorine.

Table 2.1: Oxidation potential value (source from: Effect of Hydrogen Peroxide on Industrial Wastewater Effluent, 1999)

Oxidant	**Oxidation Potential, V**
Fluorine	3.0
Hydroxyl radical	2.8
Ozone	2.1
Hydrogen peroxide	1.8
Potassium permanganate	1.7
Chlorine dioxide	1.5
Chlorine	1.4

Despite its power, H_2O_2 is a natural metabolite of many organisms, which decomposed the H_2O_2 they produce into oxygen and water. H_2O_2 is also formed by the action of sunlight on water; a natural purification system for our environment. Consequently, H_2O_2 has none of the problems of gaseous release or chemical residues that are associated with other chemical oxidants. And since H_2O_2 is totally miscible with water, the issue of safety is one of concentration. Industrial strength H_2O_2 is a strong oxidizer and as such requires special handling precautions.

The fact that H_2O_2 is used for seemingly converse applications proves its versatility. For example, it can inhibit microbial growth (as in the biofouling of water circuits) and encourage microbial growth (as in the bioremediation of contaminated groundwaters and soils). Similarly, it can treat both easy-to-oxidize pollutants (iron and sulfides) and difficult to oxidize pollutants (solvents, gasolines and pesticides).

The reason why H_2O_2 can be used for such diverse applications is the different ways in which its power can be directed; termed selectivity. By simply adjusting the conditions of the reaction (e.g., pH, temperature, dose, reaction time, and/or catalyst addition), H_2O_2 can often be made to oxidize one pollutant over another, or even to favor different oxidation products from the same pollutant (Adeyinka JS and Rim Rukeh A, 1999).

Since it was first commercialized in the 1800's, H_2O_2 production has now grown to over a billion pounds per year (as 100%) (Adeyinka, 1999). In addition to pollution control, H_2O_2 is used to bleach textiles and paper products, and to manufacture or process foods, minerals, petrochemicals, and consumer products (detergents). Its use for pollution control parallels those of the movement itself; municipal wastewater applications in the 1970's; industrial waste/wastewater applications in the 1980's; and more recently, air applications in the 1990's.

2.8.3 Environmental Applications of H_2O_2

H_2O_2 applications span the range of possible media: air, water, wastewater, soils and sludges. Depending on the objective, H_2O_2 may be used either alone or in combination with other processes to enhance their performance. There are examples of the H_2O_2 application without combining with other compound.

(a) Inorganic oxidation - Oxidizes cyanides, NO_x/SO_x, nitrites, hydrazine, carbonyl sulfide, and other reduced sulfur compounds mentioned above (odor/corrosion control).

(b) Organic oxidation - Hydrolyzes formaldehyde, carbon disulfide, carbohydrates, organophosphorus and nitrogen compounds, and various water-soluble polymers; and (with catalysis) destroys phenols, BTEX pesticides, solvents, plasticizers, chelants, and virtually any other organic requiring treatment.

(c) Metals oxidation - Oxidizes ferrous iron, manganese, arsenic, and selenium to improve their adsorption, filtration, or precipitation from process waters and wastewaters.

(d) Toxicity reduction/Biodegradability improvement - With catalysis, chemically digests complex organics into smaller, less toxic and more biodegradable fragments.

(e) Disinfection/Bio-control - Checks excess biogrowth in water supplies and cooling circuits, and (with catalysis) disinfects process waters and biological effluents.

(f) Odor control - Oxidizes hydrogen sulfide, mercaptans, amines and aldehydes. H_2O_2 may be applied directly to aqueous wastes containing these odorants, or to wet scrubbers used to remove them from airstreams. If the odors are the result of biological activity, H_2O_2 may instead be added as a preventative to eliminate the anoxic conditions which favor the generation of odors.

(g) Corrosion control - destroys residual chlorine and reduced sulfur compounds thiosulfates, sulfites, and sulfides) which form corrosive acids when condensed onto processing equipment and oxidized by air.

(h) BOD/COD removal - Oxidizes both organic and inorganic pollutants which contribute to BOD and COD; catalytic, H_2O_2 may be needed to oxidize the more resistant substances. H_2O_2 may also affect BOD/COD removal by enhancing the performance of other processes.

2.8.4 Safety precaution of hydrogen peroxide

Although hydrogen peroxide and its decomposition products are not systemic poisons, contact can cause irritation. Concentration vapors irritate the mucous membranes and the eyes. Eye contact with hydrogen is particularly dangerous because corneal burns occur very rapidly. If eyes should be contacted, they should be flushed thoroughly with water. Also consult physician immediately. Safety glasses or preferably, goggles should always be worn when handling concentrated solutions.

2.9 Factors that effects the efficiency of this reaction

2.9.1 Chemical reactivity

First and foremost, it depends on the specific properties of the chemicals involved. Some chemicals react violently and very quickly, and others very slowly. The chemical reactivity is determined by the activation energy of the reaction, or the transition state energy. This is the point of highest energy reached in the reaction, and most reaction rates are determined by the reactants ability to get over this barrier. The size of the barrier is simply determined by the inherent properties of the reactants (Howari F and H Garmoon 2003).

2.9.2 Temperature

Another very important factor, and usually the easiest to control is the temperature at which the reaction takes place. Increasing the temperature of the reacts will almost always make the reaction go faster. Decreasing the temperature will slow the reaction rate. This isn't always the case, but it is true for the very large majority of reactions. Increasing the temperature will help the reactants get reach the activation energy, and get over the barrier, as discussed above.

2.9.3 Liquid mixing

Most of the processing operations depend on the effective agitation for their success. Agitation refers to the induced motion of a material in a specific way, usually in a circulatory pattern inside the reactor. A rotating agitator produces high velocity liquid streams, which move through the reactor. As the high velocity streams comes into contact with stagnant or slow moving liquid, momentum transfer occurs. Low velocity liquid becomes entrained in faster moving stream, resulting in forced diffusion and better liquid mixing.

2.9.4 Reactant concentration

The rate of a reaction is also determined by the concentration of the reactants. In most cases, the higher the concentration of the reactants, the faster the reaction (again, this is almost always true, but there are exceptions, such as radioactive decay).

2.9.5 pH

The rate of certain reactions is affected by the pH of the solution. If the reaction involves a proton, or H^+, than a more acidic solution will have a faster rate. This is really the same effect as in the previous section, "Reactant Concentration" because the pH is really just a measure of the H^+ concentration (Mcvaugh, J. and Wall, W.T., 1996). So if H^+ is a reactant, than a low pH will have a higher concentration of that reactant, making for a faster reaction. Similarly, if OH^- is a reactant, than a high pH will make the reaction go faster because at a high pH, the concentration of OH^- is large (and the concentration of H^+ is small; they are inversely proportional).

2.10 Atomic Absorption Spectrophotometer (AAS)

Atomic absorption spectrometry (AAS) is an analytical technique that measured the concentration of elements. Atomic absorption is so sensitive that it can measure down to parts per billion of a gram (dm^{-3}) in a sample. The technique makes use of the wavelengths of light specifically absorbed by an element. They correspond to the energies needed to promote electrons from one energy level to another higher energy level. Atomic absorption spectrometry has many uses in different areas of chemistry.

2.10.1 Operation of Atomic Absorption Spectrophotometer (AAS)

Atom of different elements absorb characteristic wavelength of light. Analyzing a sample is to see if it contains a particular element means using light from that element. For example with lead, a lamp containing lead emits light from excited lead atoms that produce the right mix of wavelengths to be absorbed by any lead atoms from the