CHAPTER 1

Introduction

Industry and household sometimes pour contaminate into lakes, streams, ground waters and rivers, leading to wastewater problem. To reduce this problem, oxygen releasing materials such as H_2O_2[1], MgO_2[2,3] and CaO_2[4,5,6] were applied into water resources for preliminary wastewater remediation. Although several other oxygen contained compounds can release oxygen for example Na_2CO_3, MgO_2 and CaO_2[7], there are some advantages and disadvantages of each material. CaO_2 was always selected for this issue because it is relatively low price and has a long time of application for treatment, generally, known as an oxygen releasing compound (ORC). CaO_2 powders have been widely used in agriculture, aquiculture, poultry rising, cattle breeding and medicine.[8, 9]

Calcium peroxide (CaO_2) is a white to yellow powders. It is the one element of solid inorganic peroxy compounds which can be called a "solid form" of hydrogen peroxide.[6, 10] It can generate hydrogen peroxide, which will further decompose into highly reactive hydroxyl radical and superoxide.[11] The mechanism is simply showed by Eq.1-5 below. In its normal state, CaO_2 dissolves in water to form H_2O_2 which is known to be a strong oxidant and $Ca(OH)_2$[12]

$$CaO_2 + 2H_2O \longrightarrow H_2O_2 + Ca(OH)_2 \qquad (1)$$

Calcium hydroxide can react further with CO_2 in the air to form $CaCO_3$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \qquad (2)$$

Then, H_2O_2 can release oxygen and generation of superoxide and hydroxyl radical[11] shown by equations below

$$H_2O_2 + e^- \longrightarrow {}^{\cdot}OH + OH^- \qquad (3)$$

$$\cdot OH + H_2O_2 \longrightarrow HO_2\cdot + H_2O \quad (4)^{13}$$

$$HO_2\cdot + OH^- \longrightarrow H_2O + \cdot O_2^- \quad (5)$$

The H_2O_2 will give single electron to produce $\cdot OH$ in the suspension of alkaline-earth (IIA) metal peroxide, which was demonstrate by the addition of the scavenger.

1.1 Historical Background

French chemist Louis-Jacques discovered H_2O_2 in 1818[14] and defined it as a chemical compound with formula H_2O_2 or hydrogen peroxide. It is one part of chemical compounds in which generate by two atoms of oxygen linked together by a single covalent bond. Inorganic compounds reacted with the negatively charged peroxide ion (O_2^{2-}) that may be consider as salts of the very weak acid H_2O_2; such as sodium peroxide (Na_2O_2), barium peroxide (BaO_2) and magnesium peroxide (MgO_2)[15] formerly used as a source of hydrogen peroxide. In its purity of H_2O_2, it is a slightly more viscous than water and colorless liquid. It is an environmentally friendly oxidizing agent and can be used for various applications; especially, soil and wastewater.[16,17] H_2O_2 might be the most essential bulk inorganic chemicals of the world. It's selected as one of the ''greenest''[18] because it produces only water (by-product) of its oxidation[19,20] and release high active oxygen content (about 47% was reported in other research), to from molecular oxygen.[21,22] H_2O_2 is popularly using in industrial for pretreatment of waste soil and wastewater because it can efficiently oxidize toxic chemicals such as chlorine, thiocyanate, hypochlorite, cyanide, nitrate, mercaptans and other chemicals present in the industrial wastewater.[18,23] In addition, the beauty and medical industries also use H_2O_2 as an disinfecting ingredient. Furthermore, H_2O_2 is applying to erosion and purification of electronic materials.[18]

As a result, calcium peroxide (CaO_2) seems to be an interesting source of hydrogen peroxide in terms of stability and would be a promising alternative material for contaminant biodegradation in soil and other resources. It also occupy the capacities of bleaching, deodorizing, and disinfection.[24] However, reaction rate of oxidation reaction between CaO_2 and some contaminants are slowly, nanosized CaO_2, which increase ratio of surface to volume may increase reaction rate.[25] Nanoparticle CaO_2

would be expected to provide higher rate of reaction, high active oxygen content and is exceptionally stable. When comparing with conventional CaO_2, nanoparticle CaO_2 should has a better dispersion and transportation capacity.[26,27] Applications in clean-up of industry are widely used the advantages of solid peroxide in both engineering and science.[28]

Sodium peroxide (Na_2O_2), barium peroxide (BaO_2) and magnesium peroxide (MgO_2) formerly used as sources of hydrogen peroxide. Later, there are some work reported the advantages and disadvantages among CaO_2 and MgO_2. CaO_2 showed some more benefit in terms of molecular oxygen delivery compared to MgO_2 because, generally, MgO_2 has purity only 15–25%, whereas CaO_2 has higher purity up to 60–80%. However, duration of oxygen release of H_2O_2, CaO_2 and MgO_2 can be lasted for 10, 100 and 300 days, respectively. Production cost of CaO_2 is less expensive than MgO_2, and may simply produce in the field by heating lime with hydrogen peroxide.[29] Physically of Magnesium peroxide (MgO_2) is a white to off-white color, non-odor fine powder peroxide.[30] MgO_2 is a stable oxygen releasing compound for used to reduce contaminate in groundwater and soil can increase quality of soil for plant metabolism. Because the oxygen is released slowly, it is theorized that it may then slow to eliminate the sulfate that normally presents as the terminal electron acceptor in their electron transport chain. For medical purposes, MgO_2 used as a source of oxygen for treatment and displacement of biological waste aerobic organisms because hydrocarbons in soil is disintegrated quickly in aerobic conditions. Moreover, MgO_2 can be added to fertilizer or in soil to increase speed the microscopic creature activities and to decrease the odors form in the method system.[31] It was presented to encourage aerobic microbial biodegradation of ethylbenzene, benzene, toluene, and xylene (BTEX) for 10 weeks.[6] However, less purity of MgO_2 may loss its advantage. CaO_2, which can act similar to MgO_2, with higher purity and higher surface area, would be a neat solution.

CaO_2 has been used in several applications in industry and agricultural. Olyaie et al.[26] reported the effective of CaO_2 nanoparticle on removal of arsenic from aqueous solution. As well as Qian et al.[32] which reported removal of toluene from petroleum products by using CaO_2 nanoparticles as catalyst. Moreover, CaO_2 was used for cleanup of oil spills.[33] Northup and Cassidy[34] proposed performance degradation of tetrachloroethylene ($Cl_2C{=}CCl_2$) by CaO_2 activated with EDTA chelated Fe(III). Goi et al.[2] reported that CaO_2 can be activated as catalyst for removing polychlorinated biphenyls- containing electrical insulating oil from contaminated soil efficiently. Xiang Zhang et al.[35] showed the application of Fe(II)-EDDS complex to activate with CaO_2 in the remove of organic contaminants from groundwater such as trichloroethylene was selected as the objective contaminant.

1.2 Photocatalytic application

Photocatalytic application is the promising method for the wastewater treatment system, especially in Thailand, because it can use sunlight and ambient temperature and pressure, it may be called a “green process”. Photocatalysis is a process that be related activity of semiconductor material, generally, under UV or visible light irradiation. A semiconductor includes essentially an electron occupied valence band (VB) and an unoccupied conduction band (CB). Electrons will be promoted from the VB to the CB and leave holes when receiving photons higher or equal to band gap energy. The hole at VB will behave as an oxidizing center, whilst the electron at CB will be a reducing center, when contact with other substances. This process can be used for oxidation reaction and reduction reaction depending on purpose and suitability of band position. Photocatalysts can be reused for several times. Photooxidation process is widely known for wastewater treatment. The mechanism of this process is normally occurred via hydroxyl radical produced by trapping of hydroxide ion at the VB, although some might produce by electron acceptor of oxygen at the CB. It can be used for decomposition a wide range of organic and inorganic pollutants, such as dyes, pesticides, cyanide, aromatics, alkanes, halogenated hydrocarbons, amines, mercaptans and dissolved metal compounds

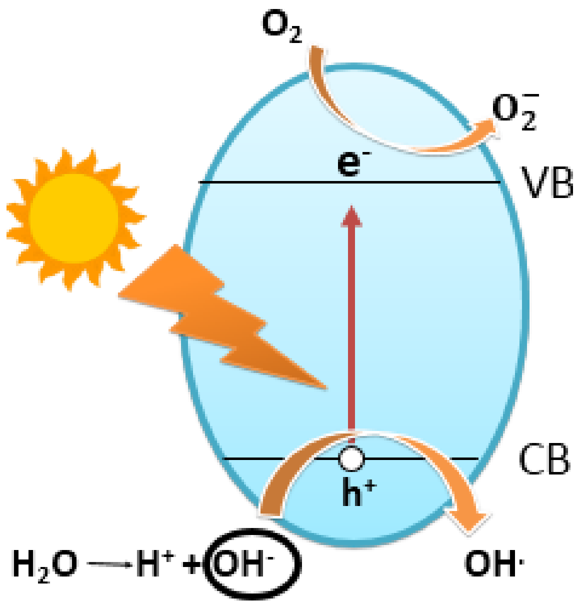

Figure 1. Reaction of photocatalytic activity

Recent studies have showed that several semiconductors (TiO_2[36,37], ZnO[38], $BiVO_4$[39], WO_3[40]) have been widely studied as photocatalysts.

Hydrogen peroxide from CaO_2 can also generate hydroxyl radicals when it is in the system that is thermodynamically favorable or under UV irradiation and plays an important role in chemical oxidation of pollutant removal as shown in Eq.6 below.[9]

$$H_2O_2 + hv \rightarrow OH^{\cdot} + OH^{\cdot} \qquad (6)$$

In this research, CaO_2 will be investigated on using as a photocatalyst under UV-visible light irradiation to destroy a wide range of organic pollutants dissolved in water because of its inexpensive.[41]

Methylene blue is generally chosen as a representative of wastewater for photocatalyst validation. Artificial sunlight source will be developed in laboratory to simulate photoactivity under sunlight.[42] Other important factors affect an efficiency of photoactivity is a recovery efficiency of material, fast recombination rate of photogenerated electron–hole pair and a low quantum yield in the photocatalytic reaction in aqueous solutions.[43] As mention aboved, a promising photocatalyst is still required to fulfill all aspects.

1.3 Photocatalytic reduction

A reduction of resazurin (Rz) is a well-known protocol to investigate photocatalytic reduction. The photoreduction activity of CaO_2 is monitored using this protocol.

Resazurin (RZ) dye is a heterocyclic N-oxide that is used to study biological materials usually. Most of these applications are based on the oxygen atom transfer reaction with the dye as donor. In this way RZ is reduced to the strongly fluorescent product resorufin (RF).[44, 45]

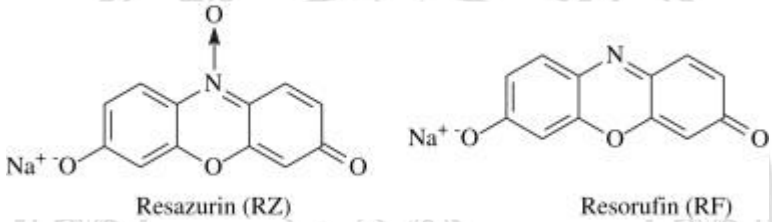

Figure 2. Resazurin and Resorufin structure

In this work, Rz will be dropped on CaO_2 before irradiation with UV or visible lamps. Color change from blue (resazurin) to pink (resorufin) would indicate a photoreduced active sample.

1.4 Disinfection[46]

In recent years, there have been some work reported that hydrogen peroxide is one of most effective disinfection procedure in water treatment. It is an exclusive oxidant, ability and environmentally friendly. In natural, oxygen and water are product of metabolism of living organisms when H_2O_2 decomposed. Properties of H_2O_2 compounds correlated to a formation of superoxide and hydroxyl radicals containing active oxygen from hydrogen peroxide solutions as shown in Eqs. (7) and (8). H_2O_2 decomposition give free radicals which are active intermediate particles formed in most cases. The process in the basic (pH>7) condition, can be expressed by Eqs. (7-12).

Formation of superoxide and hydroxyl radicals:

$$H_2O_2 + OH^- \rightleftarrows HO_2^- + H_2O \qquad (7)$$

$$HO_2^- + H_2O_2 \rightarrow OH\cdot + HO_2\cdot + OH^- \qquad (8)$$

Hydrogen peroxide decomposition:

$$HO\cdot + H_2O_2 \rightarrow H_2O + HO_2\cdot \qquad (9)$$

$$HO_2\cdot + H_2O_2 \rightarrow H_2O + O_2\uparrow + OH\cdot \qquad (10)$$

Chain termination:

$$HO\cdot + OH\cdot \rightarrow H_2O_2, \qquad (11)$$

$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2\uparrow \qquad (12)$$

Active species related to H_2O_2 can be summarized in Table 1.

Table 1. Reactive Species producing from hydrogen peroxide

Species	Species formula	Standard reduction potential (V)[48]	pH where present[49]	Role
Hydrogen peroxide	H_2O_2	1.776	pH < 11.6	Strong oxidant, weak reductant
Hydroxyl radical	$OH^{\cdot}$	2.59	pH < 11.9	Strong oxidant
Superoxide anion	$O_2^{\cdot -}$	-0.33	pH > 4.8	Weak reductant
Perhydroxyl radical	$HO_2\cdot$	1.495	pH < 4.8	Strong oxidant
Hydroperoxide anion	HO_2^-	0.878	pH > 11.6	Weak oxidant, weak reductant

Hydroxyl Radical ($OH\cdot$)[50]

Hydroxyl radical is a strong non-specific oxidant that can reacts with an organic and inorganic compound via 3 mechanisms: hydrogen abstraction, addition to multiple bonds, and direct electron transfer

Superoxide Anion ($O_2^{\cdot-}$)[51]

The Superoxide anion ($O_2^{\cdot-}$) with an acid dissociation constant (pKa) of 4.8. So, appreciable concentrations of superoxide available when the pH > 4.8.

Perhydroxyl Radical ($HO_2\cdot$)[51]

Perhydroxyl radical is the protonated form of superoxide anion ($O_2^{\cdot-}$) with a pKa of 4.8. This radical is the dominant form of superoxide present at pH < 7, for example Fenton's systems conducted at pH 3.

Hydroperoxide Anion (HO_2^-)[48]

Hydroperoxide anion is the conjugate base of hydrogen peroxide with a pKa of 11.6. It is a strong nucleophile that may readily rid contaminants.

Any choice can be found in the use of solid peroxides of alkaline-earth metals reacted with water and decompose into H_2O_2 mechanism, similar to hydrogen peroxide. It can form carbonate and hydroxide ions. Calcium peroxide decomposition process can be expressed by the following Eq.13-14 below

$$CaO_2 + 2H_2O \rightarrow H_2O_2 + Ca(OH)_2, \quad (13)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3. \quad (14)$$

High purity of nanoparticle CaO_2 is important because it is consistent to active species formation that can be used for water treatment applications, higher stability compared to other peroxides, long period of microbial disinfecting, controllable of decomposition of hydrogen, environmentally friendly and low cost.

1.5 Literature reviews

CaO_2 has been used in several applications; for example, soil and water treatment, medical, disinfection, bleaching, bioremediation and agriculture. As mentioned reasons, the new method to synthesize high purity CaO_2 would be interesting. Previously, several methods have been proposed for the production of CaO_2, those involving the use of $CaCl_2$ or $Ca(OH)_2$ as a precursor and adding reagent such as polyethylene glycol 200, sodium peroxide, ammonium hydroxide and sodium hydroxide to increase purity of CaO_2. It was found that CaO_2 was a predominant mineral product and accompanied by $Ca(OH)_2$ and $CaCO_3$ in minor compounds. The remaining was assigned to Ca and CaH_2 that present in the sample as impurities. These precursors show some disadvantage on purity control, moreover, these precursor ($CaCl_2$ or $Ca(OH)_2$) are slightly more expensive than $Ca(NO_3)_2$.

There has been several works study on synthesis of calcium peroxide (CaO_2) for use as oxygen-releasing material because CaO_2 is suitable choice for contaminant biodegradation in soil and ground water. Co-precipitation method using $CaCl_2$ or $Ca(OH)_2$ as precursor was normally used for CaO_2 preparation. There has been some report proposed the mixing of $Ca(OH)_2$ and H_2O_2 under acidic condition (pH=6 by HCl) for the production of CaO_2, the obtained powder was washed several times by distilled water and was dried at 30^{o}C for 24h. However, it was found that most particles are large and there was significant amount of impurities such as $Ca(OH)_2$ and $CaCO_3$ that were always observed from XRD result.[9]

Some reports have changed precursor to $CaCl_2$ and dissolved in distilled water and NH_4OH. After that, H_2O_2 was added. The temperatures of solution have been varied at 0, 5, 10, 50, 60, 65 and 70 ^{O}C. Finally, the powder was washed several times by distilled water and NH_4OH. It was found that this method still has low percentage yield and shows several minor components when dried higher than 100^{O}C. Octahedral crystal plates of freshly precipitated $CaO_2{\cdot}8H_2O$ was obtained from cold solution (0°C) whereas the morphology of the eight-sided plates can be seen when precipitated from hot solution (70 °C). It was surprising that the CaO_2 precipitated in the form of spheres instead of well-defined crystals.[10] Several studies have reported that addition of CaO_2

in saturated soil and ground water is a suitable choice for contaminant degradation. CaO_2 is often used as an alternative oxidant to promote organic pollutant degradation in contaminated soil. Develop a method for increasing the oxygen level of sediments and the hypolimnion using granulated CaO_2 as a compound for the slow release of oxygen and improve efficiency was also revealed.[12]

Polyethylene glycol 200 has been used to modify matrix of $CaCl_2$ precursor to achieved nanoscale CaO_2. However, $Ca(OH)_2$ and $CaCO_3$ were identified in the synthesized products, along with small quantities of inorganic CaH_2 as impurities.[11] Effect of Na_2O_2 along with H_2O_2 on purity of CaO_2 has been reported. $CaCl_2$ and Na_2O_2 would increase 80% purity of CaO_2. However, the solution has to be maintained at low temperature 2 ^{O}C for a long time.[13]

Therefore, an alternative precursor for production of CaO_2 will be validated, especially $Ca(NO_3)_2$, because it can produce high purity CaO_2 in short time and less impurity. Furthermore, it is an endothermic reaction leading to the ease of reaction controllable. In this research, a productive method to synthesize high purity nanoparticle CaO_2 using several precursor as an alternative and effective precursor under mild condition is reported. And adding additive ethanol, ascorbic acid, triton-x use for cosolvent plays a major role to adjust size of nanoparticles. The synthesized CaO_2 powders were characterized by XRD, SEM, TEM and BET techniques

1.6 Research objective

1) To synthesize high purity CaO_2 prepared by $Ca(NO_3)_2$ as a precursor

2) To study physical properties and chemical properties of CaO_2

3) To study the oxygen releasing of CaO_2