Preparation, Characterization and Application of Nanoparticles Iron Oxide Catalyst for the Treatment of Sulfidic Wastewater

by

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Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

May 2009

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

CHE MOHD SHAZLI BIN ISA

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CHAPTER 1 : ABSTRACT

Iron oxide nanoparticles were prepared by chemical reaction of iron chloride and ammonium hydroxide. The product were characterized by SEM, indicating that the fine particles are nanometer of iron oxides. The produced iron oxide nanoparticles can be act as a catalyst. It was shown by the rate of the oxidation of the sodium sulfide in the wastewater by hydrogen peroxide is higher in the presence of iron oxide nanoparticles. For the oxidation of sodium sulfide by hydrogen peroxide in the presence of iron oxide nanoparticles, the optimum condition at which the rate of the oxidation is higher were investigated by investigating the effect of the parameters of initial sulfide concentration, catalyst loading, and temperature of the system.

CHAPTER 2 : PROBLEM STATEMENTS AND OBJECTIVES

Hyperfine iron oxide nanoparticles have good performances such as magnetism, catalysis, gas-sensitivity and are widely applied in various fields. Because of its increasingly important, the objective of my project is to study the new method used to synthesize the iron oxide nanoparticles by using ferric chloride and ammonium hydroxide.

There are many applications of the iron oxide nanoparticles because of its good properties. One of its applications is as a catalyst. So, the objective of the project also is to study the effectiveness of the iron oxide nanoparticles prepared as a catalyst which is being used as a catalyst in the oxidation of the sodium sulfide from wastewater using hydrogen peroxide. At the same time, the objective also is to find the optimum condition at which the oxidation rate is higher by investigating the effects of sulfide initial concentration, catalyst loading, and temperature of the system towards the rate of the oxidation.

CHAPTER 3 : LITERATURE REVIEW

Nanoparticles of magnetic iron oxide (maghemite, Fe_2O_3 and magnetite, Fe_3O_4), which are representative magnetic materials, have become increasingly important, and many synthesize methods have been developed by the scientists for the preparation of iron oxide nanoparticles.

3.1 The Methods of Preparation of Ferric Oxide Nanoparticles.

The scientits have classified the synthesis methods into those that produce magnetic nanoparticles from solution techniques and from aerosol/vapour phases.

3.1.1 Precipitation from Solution.

In general these methods allow the preparation of magnetic nanoparticles with a rigorous control in size and shape in a simple rather way. Uniform particles are usually prepared via homogeneous precipitation reactions, a process that involves the separation of the nucleation and growth of the nuclei . In a homogeneous precipitation, a short single burst of nucleation occurs when the concentration of constituent species reaches critical supersaturation. Then, the nuclei so obtained are allowed to grow uniformly by diffusion of solutes from the solution to their surface until the final size is obtained. The most important methods described in the bibliography to obtain uniform iron-based nanoparticles in solution are briefly described in the following sections: coprecipitation, microemulsions, and decomposition of organic precursors.

Coprecipitation.

There are two main methods for the synthesis in solution of magnetic spherical particles in the nanometer range. In the first, ferrous hydroxide suspensions are partially oxidized with different oxidizing agents . For example, spherical magnetite particles of narrow size distribution with mean diameters between 30 and 100 nm can be obtained from a Fe(II) salt, a base and a mild oxidant (nitrate ions) . The other method consists in ageing stoichiometric mixtures of ferrous and ferric hydroxides in aqueous media, yielding spherical magnetite particles homogeneous in size .In addition, it has been shown that by adjusting the pH and the ionic strength of the precipitation medium, it is possible to control the mean size of the particles over one order of magnitude (from 15 to 2 nm) . The size decreases as the pH and the ionic strength in the medium increases . Both parameters affect the chemical composition of the surface and consequently, the electrostatic surface charge of the particles. Under these conditions, magnetite particles are formed by aggregation of primary particles formed within an $Fe(OH)_2$ gel. This is an ordered aggregation that gives rise to spherical crystalline particles . The smallest particles can also be generated after adding polyvinylalcohol (PVA) to the iron salts . A typical microstructure of magnetic nanoparticles produced by this method is shown in figure 1.

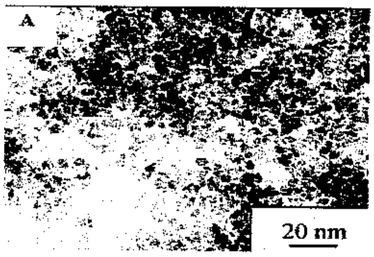

Figure 1 : Iron oxide nanoparticles prepared in solution by coprecipitation.

Microemulsions.

Water-in-oil (W/O) microemulsions (i.e. reverse micelle solutions) are transparent, isotropic, thermodynamically stable liquid media. In these systems, fine microdroplets of the aqueous phase are trapped within assemblies of surfactant molecules dispersed in a continuous oil phase. The surfactant-stabilized microcavities (typically in the range of 10 nm) provide a confinement effect that limits particle nucleation, growth, and agglomeration . W/O microemulsions have been shown to be an adequate, versatile, and simple method to prepare nanosized particles. The scientist prepared nanosized magnetic particles with average sizes from 4 to 12 nm and standard deviation ranging from 0.2 to 0.3 using microemulsions. A ferrous dodecyl sulfate, $Fe(DS)_2$, micellar solution was used to produce nanosized magnetic particles whose size is controlled by the surfactant concentration and by temperature. A typical microstructure of magnetic nanoparticles produced by this method is shown in figure 2. Magnetite nanoparticles around 4 nm in diameter have been prepared by the controlled hydrolysis with ammonium hydroxide of

$FeCl_2$ and $FeCl_3$ aqueous solutions within the reverse micelle nanocavities generated by using AOT as surfactant and heptane as the continuous oil phase

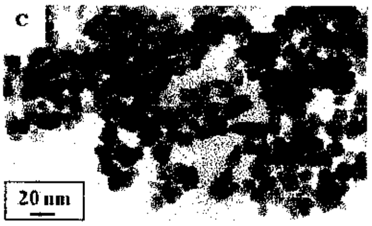

Figure 2 : Iron oxide nanoparticles prepared in solution by microemulsions.

High-temperature decomposition of organic precursors.

The decomposition of iron precursors in the presence of hot organic surfactants has yielded markedly improved samples with good size control, narrow size distribution and good crystallinity of individual and dispersible magnetic iron oxide nanoparticles. For example, scientist have demonstrated that injecting solutions of $FeCup_3$ (Cup: *N*-nitrosophenylhydroxylamine) in octylamine into long chain amines at 250–300°C yields nanocrystals of maghemite. These nanocrystals range from 4 to 10 nm in diameter, are crystalline, and are dispersable in organic solvents (figure 3). The scientist also been able to prepare monodisperse maghemite nanoparticles by a non-hydrolytic synthetic method. For example, to prepare maghemite nanoparticles of 13 nm (figure 3), $Fe(CO)_5$ was injected into a solution containing surfactants and a mild oxidant (trimethylamine oxide).

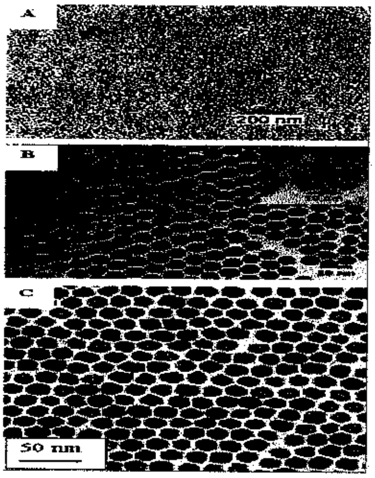

Figure 3 : Iron oxides nanoparticles prepared in solution by decomposition at high temperature of organic precursors: (*a*) $FeCup_3$. (*b*) $Fe(CO)_5$. *c*) Fe(III) acetylacetonate

Sonochemical-assisted synthesis has also been reported as an adequate method for the production of magnetite and maghemite nanoparticles. In sonochemistry, the acoustic cavitation, that is, the formation, growth, and implosive collapse of a bubble in an irradiated liquid, generates a transient localized hot spot, with an effective temperature of 5000K and a nanosecond lifetime The cavitation is a quenching process, and hence the composition of the particles formed is identical to the composition of the vapour in the bubbles, without phase separation.

Electrochemical methods have also been used for the production of maghemite nanoparticles . The electrochemical synthesis of nanoparticles of γ -Fe_2O_3 was performed in an organic medium. The size was directly controlled by the imposed current density, and the resulting particles were stabilized as a colloidal suspension by the use of cationic surfactants. The size distributions of the particles were narrow, with the average sizes varying from 3 to 8 nm.

3.1.2 Aerosol/vapour methods.

Spray and laser pyrolysis have been shown to be excellent techniques for the direct and continuous production of well-defined magnetic nanoparticles under exhaustive control of the experimental conditions. Their high-production rate can anticipate a promising future for the preparation of magnetic nanoparticles. The main difference between spray and laser pyrolysis is the final state of the ultrafine particles. In spray pyrolysis, the ultrafine particles are usually aggregated into larger particles, while in laser pyrolysis the ultrafine particles are less aggregated due to the shorter reaction time.

Spray pyrolysis.

Spray pyrolysis is a process in which a solid is obtained by spraying a solution into a series of reactors where the aerosol droplets undergo evaporation of the solvent and solute condensation within the droplet, followed by drying and of the precipitated particle at higher temperature . This procedure gives rise to microporous solids, which finally sinter to form dense particles. This method represents a convenient procedure for obtaining finely dispersed particles of predictable shape, size, and variable composition.

The resulting powders generally consist of spherical particles, the final diameter of which can be predetermined from that of the original droplets. The method offers certain advantages over other more commonly used techniques (such as precipitation from homogenous solution) as it is simple, rapid, and continuous..

Most of the pyrolysis based processes employed to produce maghemite nanoparticles start with a Fe^{3+}salt and some organic compound that acts as the reducing agent. It was shown that in this procedure Fe^{3+} is partially reduced to a mixture of Fe^{2+} and Fe^{3+} in the presence of organic compounds with the formation of magnetite, which is finally oxidized into maghemite. Without the presence of a reducing agent, hematite is formed instead of maghemite . In alcoholic solutions, uniform γ -Fe_2O_3 particles can be prepared with a wide variety of particle morphologies and sizes, ranging from 5 to 60 nm, depending on the nature of the iron precursor salt . A schematic representation of the device used is given in figure 4.

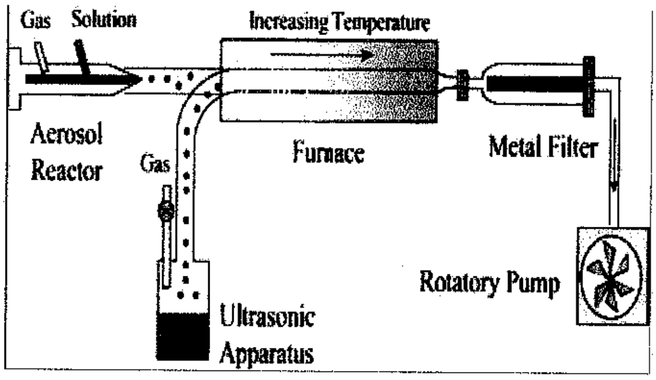

Figure 4 : Spray pyrolysis device

The device essentially consists in an aerosol droplet generator (atomizer, ultrasonic, etc), a furnace and a particle recovery system. Dense aggregates with spherical shape composed of γ -Fe_2O_3 subunits with a mean diameter of 6 and 60 nm have been obtained using Fe(III) nitrate and Fe(III) chloride solutions, respectively. On the other hand, γ -Fe_2O_3 obtained from acetylacetonate solutions resulted in monodispersed particles of about 5 nm in diameter while maghemite particles derived from Fe(II) ammonium citrate appeared as hollow spheres with a mean diameter of 300 nm. The latter consisted of small crystallites aggregated forming a shell, the size of which varied between 10 and 40 nm, depending on the heating temperature in the furnace. A typical microstructure of magnetic nanoparticles produced by this method is shown in figure 5.

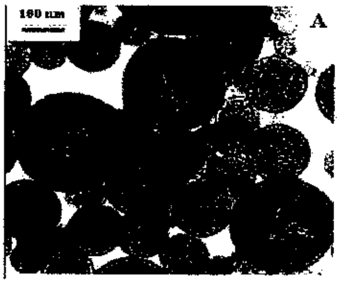

Figure 5 : Magnetic nanoparticles of iron oxides prepared by spray pyrolysis.

Laser pyrolysis.

The method involves heating a flowing mixture of gases with a continuous wave carbon dioxide laser, which initiates and sustains a chemical reaction. Above a certain pressure and laser power, a critical concentration of nuclei is reached in the reaction zone, which leads to homogeneous nucleation of particles that are further transported to a filter by an inert gas. Three characteristics of this method must be emphasized: (a) the small particle size, (b) the narrow particle size distribution, and (c) the nearly absence of aggregation. Pure, well-crystallized and uniform γ -Fe_2O_3 nanoparticles can be obtained in one single step by a CO_2 laser pyrolysis method (figure 6). Samples with particles of 3.5 and 5 nm in size and very narrow size distribution have been obtained under different experimental conditions

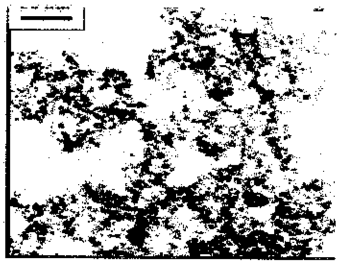

Figure 6 : Magnetic nanoparticles of iron oxides prepared by laser pyrolysis.

To obtain the γ -Fe_2O_3 nanoparticles $Fe(CO)_2$ (iron) was used as precursor. Due to the fact that this precursor does not absorb the radiation at the laser wavelength 10.60 ± 0.05μm), ethylene was used as absorbent as well as the carrier to transport the carbonyl vapour to the reaction zone. Ethylene does not decompose at the energy density used (652Wcm−2) but simply absorbs the laser radiation heating the iron pentacarbonyl, which is decomposed into iron and carbon monoxide. In order to obtain iron oxide, air has to be introduced into the system, either with the iron pentacarbonyl vapour causing oxidation under the laser radiation or mixed with argon.

In this project also, one of the applications of the ferric oxide nanoparticles was investigated as a catalyst to remove the sulfidic wastewater by using hydrogen peroxide.

3.2 The Methods used to remove Sulfide Compounds in the Wastewater.

There are various technologies are used for the removal of the sulfides. For convenience it has been divide into the following two main groups.

(1) Vapor phase technologies (2) liquid phase technologies.

3.2.1 Vapor Phase Technologies

Vapor phase technologies ventilate the point sources of odor problems. This technology is used for the air treatment and waste water both treatments. Following are the sub technologies working on the principles of vapor phase technologies.

(a) Wet scrubbing (b) Liquid redox technology (c) Biofiltration
(d) Scavengers (e) Carbon adsorption.

Wet scrubbing

Wet air scrubbing is the most flexible and reliable technology for vapor phase wastewater odor control. Besides sulfides this technology can be used to treat virtually any water-soluble contaminant. In a wet air scrubber the odor contaminants are solubilized from the vapor phase into an aqueous chemical solution .The removal mechanism is purely chemical .One of the major advantage of wet scrubbing systems is the reliability and flexibility provide by the use of chemicals and chemical reactions.

A major challenge in the design and operation of wet air scrubber is the minimization of chemical use and cost while maintaining complete flexible and reliable treatment. As mentioned, the major source of unpleasant smell is hydrogen sulfide which can be removed by wet scrubbing technology.

Liquid redox technology

Liquid redox technology has a relatively long history, but is not widely used in the odor control market because high capital cost .Liquid redox units use chelated metals dissolved in water solution to remove sulfides from a gas stream and convert it into catalytically to solid ,elemental sulfur. The metal ion in the solution removes electrons(negative charges) from a sulfide ion (s-) to form sulfur and in turn can transfer electrons to oxygen in the regeneration process. Although there are many metals that can perform these functions, iron is the most commercially used metal because it is relatively inexpensive and nontoxic. Liquid redox processes have limited applications in waste water treatment facilities compared to wet scrubber, as they have higher capital costs. But liquid redox units have less operating cost as compared to the other vapor phase treatment options. Therefore in cases where concentration of hydrogen sulfide is greater , there this technology can be applied economically.

Biofilteration

Biofilteration technology can be used to treat a variety of biodegrable and water soluble contaminats. In a biofilter, the odor contaminants are solubilized from the vapor phase into an aqueos phase on the surface of an organic medium such as compost, mulch or peat. The compounds are then degraded by the bacteriological population on this media. Biofilters are very effective at removing sulfur based odor compounds such as hydrogen sulfide, organic sulfides, inorganic sulfides and mercaptans.

Scavenger

Scavangers are solid or liquid materials that remove sulfur compounds from gas or liquid streams, reacting with them and converting them to stable compounds. In this the media is completely consumed , therefore scavengers are used for low levels of contaminants.

Carbon adsorption

This system is only applicable for the treatment of the vapor phase stream (air stream).For sulfide removal from waste water this system can be used in combination with other systems. In this system the air stream is passed over a bed of adsorbent(carbon) and the odor causing compounds are attracted to and adhere to the surface of the adsorbent.

3.2.2 Liquid Phase Technologies

Liquid phase technologies involve the treatment of a waste water stream to control the release of odor and corrosion causing compounds from the stream. Most liquid phase technologies involve the addition of a chemical to the waste water to either control the formation of odorous compounds or react with those compounds once they are formed . Liquid phase treatment not only controls the odor, but it provides corrosion control in addition to odor control. . Following are the sub technologies working on the principles of liquid phase technologies.

(a) iron salts (b) bioxide process (c) anthraquinone (d) oxidizing agents.

Iron salt

Iron salts are applied to waste water to oxidize or precipitate dissolved sulfides. Ferrous salts such as ferrous sulfate precipitate sulfides as ferrous sulfide. Ferric salts such ferric chloride oxidize some of the sulfide to sulfur while reducing the ferric iron to ferrous iron. The remaining ferrous iron then reacts with dissolved sulfide to form the ferrous sulfide precipitate. Ferrous sulfide is alight precipitate, black in color that is carried downstream to the treatment plant. With the aeration process of the treatment plant the ferrous sulfide is dissociated. The sulfide is oxidized to sulfate and the ferrous iron is oxidized to ferric iron. The ferric iron can then be used for chemical precipitation of phosphorous. Iron salts are specific to dissolve sulfides.

Bioxide process

The bioxide process involves the application of nitrate solution (bioxide) to wastewater. It is a patented process, proprietary toUS filter. The process uses naturally occurring bacteria to biochemically oxidize dissolved sulfide. The sulfide typically is either generated upstream of the injection point where nop nitrate exists in the waste water or is contributed downstream via aseptic lateral flow. Nitrate is injected in sufficient quantities to biochemically oxidize the sulfide via the following reaction.

$$8NO^{-3} + 5H_2S \rightarrow 5SO^{4-} + 4N_2 + 4H_2O + 2H^+$$

The reaction takes place in the bulk flow and in the upper zones of the slime layer. Nitrate is not added in sufficient quantities to fully saturate the slime layer, therefore sulfide production continues to occur in the lower zone of the slime and is removed in the upper zones or in the bulk flow. The bioxide solution is not classified as a hazardous compound . It is relatively easy and safe to store, handle and apply.

Anthraquinone

Anthraquinone is a chemical compound that interrupts the sulfate reduction process carried out by sulfate reduction bacteria in waste water under anaerobic conditions. This metabolic process occurs in the cytoplasm of the bacteria. Anthraquinone interacts with the cytoplasm of the bacteria and disrupts the sulfate reduction process. Anthraquinone is a none hazardous compound .

Oxidizing agents

In many cases it has been observed that the major source of unpleasant smell is hydrogen sulfide, which can be removed by wet scrubbing in aqueous sodium Hydrate but presence of Sodium sulfide in waste water provides a source of hydrogen sulfide. So if sodium sulfide is oxidized completely in an aqueous alkaline solution, then the major source of unpleasant smell hydrogen sulfide will not be generated . Oxidation for waste water odor control involves the application of a strong chemical oxidizing agent to the waste water. The oxidizing agent is used to chemically react with dissolved sulfides, converting it to sulfate or sulfur .The common oxidizing agents are hydrogen peroxide, ozone, permanganate, air and hypochlorites. Air is the naturally available oxidant .It is mostly used as an oxidant with a catalyst.

Coal flash has been used as a catalyst in the oxidation of aqueous sodium sulfide in the temperature renage of 303 to 333k. The deactivation of the catalytic effect of fly ash was found to be less than 31% after the fifth repeated use. The reaction is controlled by both the film diffusion and interparticle diffusion .Sulfides and sulfates can be removed by stripper. In one process air and waste water are passed in counter current direction through a stripper in which 60 to 70% of sulfides are removed .After this process the waste water is treated in an aerobic system before the final disposal .The parameters involved in the design and operation of stripper are liquid flow rate, air flow rate, liquid to air ratio and ph profile are optimized .One of the problem of the anaerobic waste water treatment system is the formation of sulfide upon the reduction of the sulfate and other sulfur containing compounds .Release of sulfide is undesirable because of its smell ,toxicity and corrosive properties. Sulfide removal by direct introduction of air into anaerobic bioreactor system has been investigated .Sulfide oxidation proceeds both biologically and chemically. Biological oxidation in waste water is typically associated with the activity of colorless sulfur bacteria .These bacteria utilize the energy derived from the following overall reactions.

$$2HS^- + O_2 \rightarrow 2S^\circ + 2OH^- \quad DG^\circ = -169.4\ kJ/mol$$

$$2HS^- + 4O_2 \rightarrow 2SO_4^- + 2H^+ \quad DG^\circ = -\ 732.6\ kJ/mol$$

Both biological and chemical oxidation is believed to start with formation of the polysulfides which can be protonated to elemental sulfur. Further oxidation will gives rise to the formation of the thiosulfates and sulfates. In order to obtain an effective sulfide oxidation in microaerobically operated waste water treatment system sulfide oxidation should be effective in competition for oxygen with other oxidative processes such as aerobic oxidation of the organic cod . For effective sulfide oxidation ,oxidation of sulfide should be faster than the reduction of oxidized sulfide species .One of the methods of removal of sodium sulfide from wastewater is treating the wastewater with hydrogen peroxide at freezing point. The reaction was found to be accelerated by freezing. The reaction rate at freezing point was found five times faster than at 25C°.

The decomposition of sulfide by freezing obeys zero-order kinetics, and the rate coefficient was 11.9-mol dm^{-3} min^{-1} at a freezing rate of 0.83-cm3 min^{-1}. Zero-order kinetics is one of the characteristics of freezing rate-controlled reactions. Thiosulfate, sulfite, and an unknown sulfur compound were also observed as intermediates in the reaction by freezing. The decomposition of thiosulfate obeys first-order kinetics, and the rate coefficient was 0.0496 min^{-1} at -15°C. The rate coefficient in freezing at -15°C is about 47 times faster than that in solution at 25°C. Sulfide, thiosulfate, and sulfite were consumed after 90 min. However, the unknown sulfur compound was not oxidized and was preserved in ice for a long time even in the presence of an excess of hydrogen peroxide. The concentration of an unknown sulfur compound in the frozen sample can be changed by changing the concentration of H_2O_2 and the pH of the solution. Freezing could be used for rapid preparation and preservation of unstable substances in solution

But problems are present with this method because if these methods are applied to waste water treatment, some part of the toxic substances of the catalyst such as heavy metals etc will dissolve in waste water. In addition there will be economical difficulties in applying these methods to a very large continuous flow of industrial wastewater.

3.3 The Oxidation of Sodium Sulfide using Hydrogen Peroxide in the presence of Ferric Oxide

In my project, I studied the alternative method of sodium sulfide removal from the wastewater by treating sodium sulfide with hydrogen peroxide in the presence of ferric oxide. In this oxidation process, the sulfide compounds react with oxidizing agent, that is hydrogen peroxide and converted to the sulfate according to the reaction below

$$S^{-2} + 4H_2O_2 \rightarrow SO4^{-2} + 4H_2O$$

$$SO_3^{-2} + H_2O_2 \rightarrow SO_4^{-2} + H_2O$$

$$HSO_3^{-2} + H_2O_2 \rightarrow HSO_4^{-} + H_2O$$

The presence of Ferric oxide is to increase the rate of the reaction. In order to investigate the optimum condition at which the rate of oxidation is higher, a series of experiment will be carried out at different parameters of initial sulfide concentration, hydrogen peroxide dosing, ferric oxide loading, and temperature of the system

CHAPTER 4 : METHODOLOGIES

4.1 Preparation of Iron Oxide nanoparticles.

Iron oxide particles were synthesized from ferric chloride solution and ammonium hydroxide. 2.5% ferric chloride solution was prepared by dissolving 2.027g of ferric chloride powder in 500 ml of distilled water. 2.5g of citric acid was then added into 100ml of ferric chloride solution in a stirred beaker. The ammonia solution was added into the solution until the pH of the solution become 9. The gel mass formed was taken into crucible and warmed up in a dryer at 120^0C . After that, the sample obtained was grounded in a mortar pestle and was heated up in a furnace at 800^0C for 1 hour. Finally, the iron oxide particles obtained were characterized using Scanning Electron Microscopy (SEM) to check the size of the particles.

4.2 Oxidation of Sodium Sulfide in the Wastewater.

A measured quantity of ferric oxide (catalyst) was added to the sulfide solution in the stirred beaker followed by addition of hydrogen peroxide. Samples were drawn from time to time to measure the concentration of the sulfide. This method was repeated to investigate the effect of the catalyst loading, initial sulfide concentration, hydrogen peroxide dosing, and temperature of the system. The graphs of sulfide concentration versus time were plotted for each parameters investigated.

CHAPTER 5 : RESULTS AND DISCUSSIONS

The sample prepared by the reaction between ferric chloride and ammonium hydroxide is shown in figure 7.

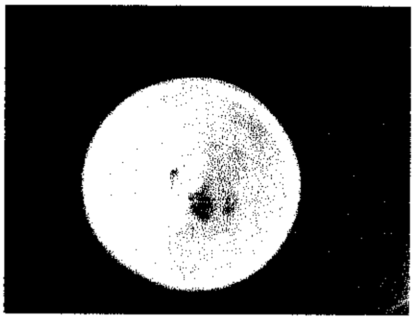

Figure 7 : Iron oxide nanoparticles

The colour of the sample obtained is red-brown. It indicates that the sample formed is iron oxides. The reaction of the formation of iron oxides is as follows :

Iron Chloride + Ammonium Hydroxide → Iron Oxide + Ammonium Chloride

The SEM photograph of the iron oxides obtained is presented in figure 8.

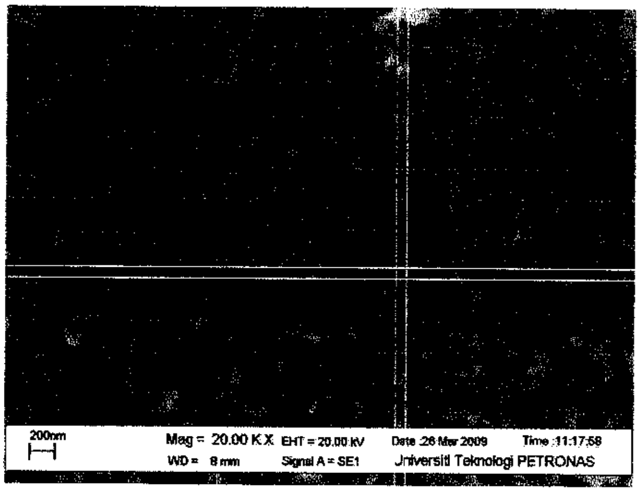

Figure 8 : SEM micrograph of iron oxide particles

From the micrograph, the size of the iron oxides is 85nm . It means the iron oxides prepared are in the range of nano size (1nm-100nm). So, it proves that the product obtained are nanoparticles of iron oxide.

The iron oxide nanoparticles have many applications and are widely used in many industries. One of its applications is as a catalyst. So, in the project also, I did a research to show that the iron oxide nanoparticles formed can be act as a catalyst by doing the oxidation process of sodium sulfide in the wastewater using hydrogen peroxide.

The reaction between sodium sulfide and hydrogen peroxide follows the chemical reaction below :

$$Na_2S + 4H_2O_2 \rightarrow Na_2SO_4 + 4H_2O$$

To investigate the iron oxide nanoparticles can be act as a catalyst, the oxidation processes were done at different iron oxide nanoparticles loading, but the other parameters such as the initial sulfide concentration, temperature of the system and hydrogen peroxide dosing were kept constant. The figure below shows the results obtained :

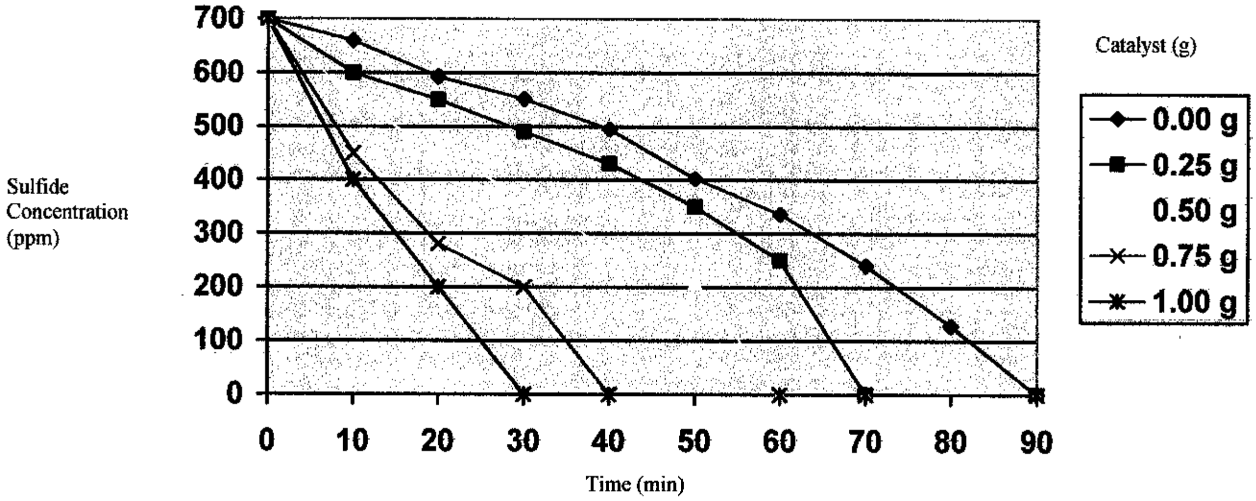

Figure 9 : The graph of sulfide concentration versus time for different catalyst loading

From the graph above, when the iron oxide nanoparticles were added into the solution, the slope of the graph become higher and the time for the complete removal of the sulfide concentration become shorter. It shows that the iron oxide nanoparticles increase the rate of the oxidation. So, it proved that the iron oxides nanoparticles can be act as a catalyst.

From the graph also, when the catalyst loading is higher, the rate of the oxidation also is higher. This is because when the amount of the catalyst is increases, the catalyst surface area provided to the reaction also increases and subsequently the rate of the oxidation will increase.

To determine the effects of the sulfide initial concentration towards the rate of the oxidation, the experiments were done at different value of the sulfide initial concentration while the other parameters such as iron oxide nanoparticles loading, system temperature and hydrogen peroxide dosing were kept constant.

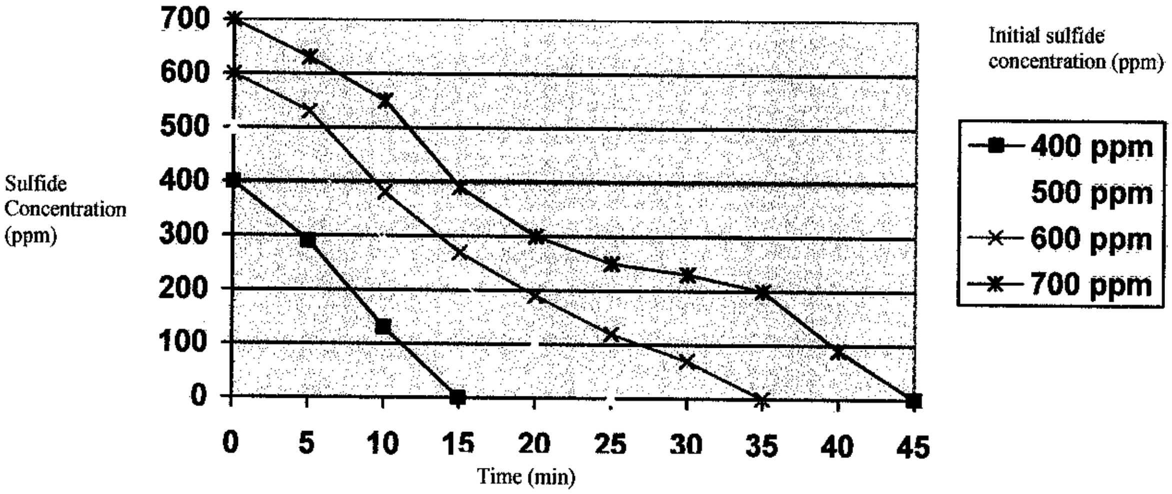

Figure 10 : The graph of sulfide concentration versus time for different sulfide initial concentration

The plots show that the slope of the graph is increases when the initial concentration of the sulfide decreases. It means that the rate of the oxidation is higher at lower initial concentration. The rate of sulfide removal is inversely proportional to the initial sulfide concentration.

The temperature of the system also will affect the rate of the oxidation process. To prove it, the variable of the temperature of the system was changed while the other parameters such as the iron oxide nanoparticles loading, initial sulfide concentration and hydrogen peroxide dosing were kept constant.

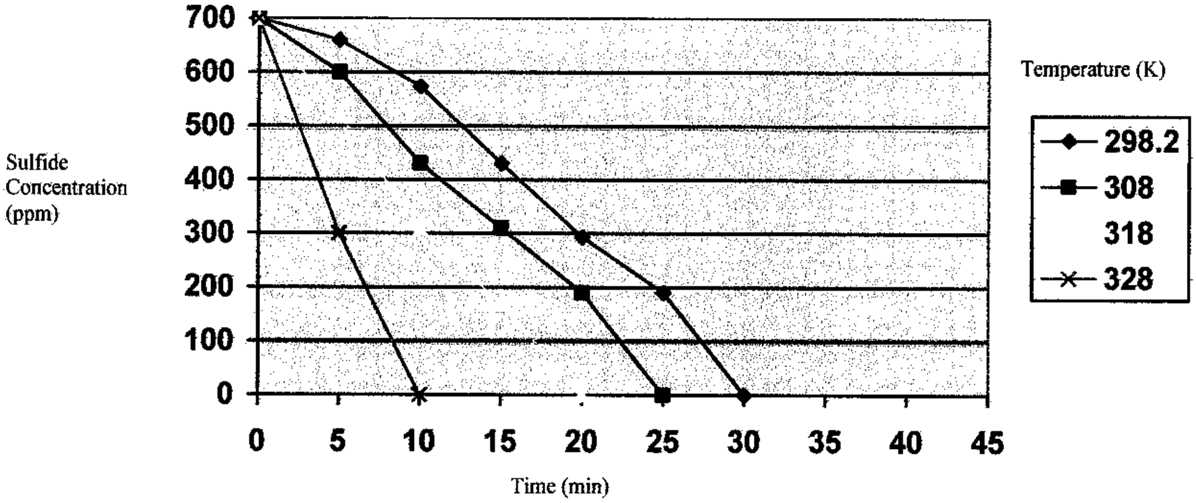

Figure 11 : The graph of sulfide concentration versus time at different system temperature

The graph shows when the temperature of the system is increases, the slope of the graph also increases, and the time for the complete removal of the sulfide is decreases. It shows that the rate of the oxidation is higher at the higher temperature. This is because, when the temperatuate of the system is higher, the molecules of the reactants will have higher kinetic energy, so the reactants molecule will collide more frequently to each other and finally the rate of the oxidation is increases.

CHAPTER 6 : CONCLUSION

The nanoparticles of iron oxide were prepared by the chemical reaction of iron chloride and ammonium hydroxide. The product obtained is red-brown in colour shows that the compound formed is iron oxides. The iron oxides were then characterized by SEM shows it is in nano range of size, that is about 85nm.

The results of the oxidation of sodium sulfide in the wastewater using hydrogen peroxide show the rate of the oxidation is higher in the presence of iron oxide nanoparticles. It means the iron oxide nanoparticles can be act as a catalyst which is to increase the rate of the reaction.

For the oxidation of sodium sulfide using hydrogen peroxide in the presence of iron chloride, it shows the hazardous sulfide compounds were converted to the sulfate compounds that is less hazardous. It was demonstrated by the concentration of the sulfide is decrease over the time. From the studying of the effects of the parameters, it shows that the optimum condition at which the rate of the oxidation is higher when the initial concentration of sulfide concentration is lower, the catalyst loading is higher and the system temperature is higher.

REFERENCES

1.) Nanostructure : Synthesis, Functional Properties and Applications by Thomas Tsakalakos, Ilya A. Ovid'ko and Asuri K. Vasudevan, NATO Science Series

2.) Nanostructured Materials by Jackie Y. Ying, ACADEMIC PRESS

3.) Nanocrystalline Metals and Oxides, Selected Properties and Applications by Philippe Knauth and Joop Schoonman, Kluwer Academic Publishers

4.)http://www.chemicalland21.com/arokorhi/industrialchem/inorganic/SODIUM%20SULFIDE.htm

5.) http://www.chiyoda-corp.com/biz/e/environ/polysul/ps-e.shtml

6.) http://www.ejournalnet.com/Contents/Issue_1/7/7_2001.htm

7.) http://www.jtbaker.com/msds/englishhtml/s5042.htm

8.)http://www.merichem.com/products_services/refining_technology/product_literature/mericon/effluent_caustic/effluent_caustic6.php

9.) http://www.uop.com/objects/5%20Sulfide%20Oxidation.pdf